

## DIAMOND DEPOSITION ON METALS FROM THE VAPOUR PHASE: NUCLEATION, GROWTH AND ADHESION STUDIES

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**Abstract.** Thin polycrystalline films of diamond have been deposited onto various substrates including copper, stainless steel, titanium and chromium using hot filament and microwave plasma enhanced chemical vapour deposition processes. Surface pre-treatments used to enhance diamond nucleation included polishing using a range of abrasives of different sizes, ultrasonic cleaning and negative biasing. Furthermore, a new approach of further increasing the diamond nucleation density has been presented, which amalgamates both substrate polishing and biasing. Biasing produced broad *D*- and *G*-bands of microcrystalline graphite, as evident from the Raman spectrum. The material formed after the biasing process consisted of a network of amorphous carbon and microcrystalline graphite phases. The *D*- and *G*-bands of microcrystalline graphite totally diminished from the Raman spectrum once the precursor material was exposed to hydrogen plasma for 10 minutes due to the etching of the graphitic phases.

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## 1. Introduction

Under normal conditions, the adhesion of diamond films on copper and stainless steel is generally very poor with films tending to peel off easily. Titanium and chromium have been investigated in this study as interlayer materials for producing adherent diamond coatings on both copper and stainless steel. Conventional adhesion test methods such as pull-off and scratch tests have been used to characterise the coating adhesion. Further, we introduce a method, which involves making steel impressions on the coatings and then uses micro-Raman spectroscopy to characterise the coating adhesion. This method is potentially interesting when non-destructive evaluation is required for quality control. These results are supplemented with data obtained from a newly proposed adhesion test method which combines indentations with acoustic emission signals during loading to characterise the adhesion. This method gives data whilst indentations are taking place and can give valuable information regarding the on-set of adhesive failure. It was observed that an indentation at 105 N load caused the film to delaminate from the Cr substrate, while the diamond film remained bonded to the Ti even after an indentation at 180 N.

Diamond coatings have attracted considerable interest from research scientists throughout the world ever since the realisation that polycrystalline diamond films can be successfully deposited onto a number of materials using a process known as chemical vapour deposition (CVD) [1, 2]. Indeed, diamond has many exceptional properties, which makes it an exciting engineering material. As a result, diamond coatings find potential uses in a diverse range of industrial applications [3]. There are however significant challenges associated with deposition of diamond on certain materials which include low diamond nucleation density, low growth rates and poor adhesion [4]. In general, diamond nucleation is highly sensitive to the conditions of the surface such as composition, roughness and orientation. To promote nucleation, several surface pre-treatment methods have been used on a number of substrate materials. The most widely used surface pre-treatment methods are substrate polishing using various abrasive powders, ultrasonic treatment and substrate biasing. Substrate biasing involves applying a negative or a positive bias voltage to the substrate and exposing the substrate surface to a plasma generated above the surface. In this study, surface polishing and negative substrate biasing have been employed separately as well as in amalgamation to optimise the diamond nucleation density. The effects of polishing duration, polishing material and ultrasonic cleaning on the nucleation density have also been investigated. Process parameters are also known to greatly influence the diamond deposition process since they alter the plasma characteristics as well as the substrate surface. In the present study, the effects of critical process parameters such as methane gas

concentration and microwave plasma power on diamond deposition have also been considered.

Since majority of the industrial applications of diamond require adherent coatings a number of attempts have been made to accomplish adequate adhesion between the diamond and substrate materials which have very little carbon affinity, such as copper, and of strong carbon dissolving, like steel. For example, Ralchenko et al [5] employed a tungsten interlayer material to improve the adhesion. Whereas, Narayan et al [6] used a pulsed laser irradiating method to provide additional energy to the incoming species in order to improve the adhesion. The latter method involved the partial melting of the copper surface layer, so that the diamond particles could be embedded into the substrate. Although many workers have employed a number of carbide forming materials as buffer layers to obtain reasonable adhesion, inadequate work has been carried out using chromium as an intermediate layer to obtain adherent diamond coatings onto copper substrates. These substrates could be potentially useful in the microelectronics industry. Titanium was also used as an intermediate layer for improving the diamond coating adhesion on copper and steel substrates.

In order to characterise the coating adhesion a number of methods have been employed, including pull-off, scratch and indentation tests [7]. The pull-off tests are accurate and quantitative. However, the main criticism attached to this method is that the tested critical force is limited by the strength of the adhesive, normally weaker than 90 MPa. Thus, the adhesive usually fails before the adhesion of the diamond coating on the substrate [7]. The adhesion scratch tests are widely used to evaluate a whole variety of hard coatings. However, the high hardness of the diamond film may lead to the cleavage of the scratch tip after a single pass, with obvious consequences on both repeatability and economics. As a comparison, the indentation tests reduce considerably the possible damage to the indenter tip and therefore are more viable for analysing the coating adhesion by comparing the dimension of the film delamination under a certain load. However, the film delamination under a high indentation load is usually accompanied by irregular film cracking, leading to difficulties in determining the delamination area and in comparing the coating adhesion. Alternatively, the coating adhesion can be compared by the critical load value that initiates the propagation of the film delamination. The present work also focuses on determining accurately the critical load by detecting acoustic emission signals during indentation tests.

## **2. Experimental**

A microwave plasma chemical vapour deposition (MPCVD) system and a hot-filament chemical vapour deposition (HFCVD) system modified to enable the

substrate to be negatively biased have been used to carry out the depositions. The HFCVD and the MPCVD systems have been described elsewhere [8]. During diamond deposition using the HFCVD process the following conditions were employed: methane ( $\text{CH}_4$ ) concentration 1%; hydrogen concentration (99%) excess; filament-substrate distance 4 mm; filament voltage 13 V, substrate temperature 1100 K, deposition pressure 20 Torr. The conditions employed when using the MPCVD process were as follows: microwave power 1200–2500 W; gas pressure 90 Torr; total gas flow rate 424 sccm consisting of 400 sccm  $\text{H}_2$  and 24 sccm  $\text{CH}_4$ ; deposition temperature  $\approx 750^\circ\text{C}$ .

Prior to diamond deposition the copper substrates were polished with a range of polishing materials of different grain sizes which included diamond powder, diamond paste, alumina paste and SiC. The substrates were then ultrasonically cleaned in acetone to remove any loose residues. Biasing experiments were conducted on a diamond-coated  $25 \times 25$  mm molybdenum substrate holder. Before biasing the filament was pre-carburised for 15 minutes under standard CVD growth conditions except at 3% methane concentration. During biasing the following conditions were employed: methane concentration 3%; hydrogen 97%; bias voltage from 0 to 300 V; emission current 100 mA; substrate temperature, 1115 K; biasing time 0–30 minutes.

Pull-off tests were conducted using a SHIMADZU AGS-5KND tension/compression tester. An epoxy cement was used to bond a cylindrical metal stud of 3 mm in diameter to the sample surface. The readings were recorded automatically by a computer during the test. The pulling force was normal to the sample surface. Scratch tests were performed using a CSEM REVTEST tester fitted with an acoustic emission (AE) sensor and analysis software. The diameter of the diamond tip used was  $200\ \mu\text{m}$ . The scratch speed was 5 mm/min and load speed 100 N/min. Chromium and titanium interlayers were deposited on copper and stainless steel substrates by means of evaporation and DC-sputtering methods. The resultant films were characterised for crystallinity, morphology and carbon-phase purity by using SEM and Raman spectroscopy.

### 3. Results and Discussion

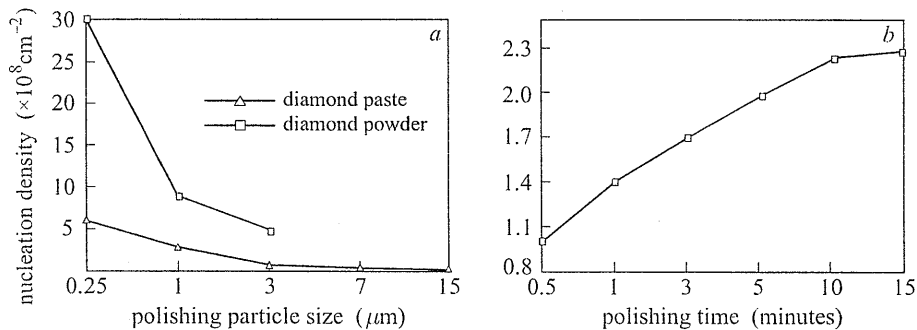
#### 3.1. Role of Surface Pre-treatment in Diamond Nucleation

Diamond deposition was carried out on copper substrates using the HFCVD system. The nucleation densities obtained on copper substrates polished with  $3\ \mu\text{m}$  diamond powder,  $3\ \mu\text{m}$  diamond paste,  $3\ \mu\text{m}$  alumina paste and silicon carbide (2400 grid) were calculated to be  $2.0 \times 10^8\ \text{cm}^{-2}$ ,  $2.93 \times 10^7\ \text{cm}^{-2}$ ,  $1.25 \times 10^7\ \text{cm}^{-2}$  and  $3.0 \times 10^6\ \text{cm}^{-2}$ , respectively (see Table 1). All the nucleation density values were calculated from the SEM micrographs. Previous

studies have shown that without any surface pre-treatment nucleation densities in the order of  $10^3$ – $10^5$   $\text{cm}^{-2}$  are possible [9–11]. It has been postulated that it is the residues, which remain behind on the substrate after the polishing process which play a critical role in initiating the nucleation process [12]. The exact mechanisms involved with the actual nucleation enhancement are still not fully understood. From our findings the effect of the polishing materials on nucleation enhancement on copper increases in the following order: diamond powder > diamond paste > alumina paste > silicon carbide. This observation is in agreement with the findings of other workers in the field [13, 14].

**Table 1**

Polishing material	Nucleation density			
	polished ( $\times 10^7$ $\text{cm}^{-2}$ )	polished + bias ( $\times 10^7$ $\text{cm}^{-2}$ )	actual increase ( $\times 10^7$ $\text{cm}^{-2}$ )	increase (%)
Diamond powder	20	27.5	7.50	38
Diamond paste	2.93	4.98	2.03	70
Alumina paste	1.25	1.50	0.25	20
SiC	0.30	0.40	0.10	33



**Fig. 1.** (a) Effect of particle size in the polishing material on diamond nucleation density for diamond powder and diamond paste  
(b) Relationship between diamond nucleation density and polishing time

The effect of particle size in the polishing material on the diamond nucleation density was also investigated. For this set of experiments, diamond powder and diamond paste were used as the polishing materials. Figure 1a shows the effect of particle size on diamond nucleation density for diamond powder and diamond paste. Generally, the nucleation densities increased as the diamond particle size for both the diamond powder and the diamond paste decreased. However, the nucleation density values were greater with the diamond powder than with the diamond paste. Therefore, diamond in the powder form is more

effective than in the paste form in enhancing diamond nucleation density. This may be due to the increased residue density obtained after polishing with diamond powder as compared to when polishing using diamond paste. The effect of polishing duration on diamond nucleation density was also investigated. The copper substrates were polished with 1  $\mu\text{m}$  diamond paste for 0.5–15 minutes followed by ultrasonic cleaning for 3 minutes. Figure 1*b* shows that the nucleation density increases with increasing polishing duration. It can be that with increasing polishing time the residue density increases and therefore greater number of diamond particles nucleate on top of these residues.

The results obtained from the investigation relating to the effect of ultrasonic cleaning duration on the nucleation density were of some interest. The copper substrates were polished with 7  $\mu\text{m}$  diamond paste for 3 minutes and ultrasonically cleaned in acetone for 3 minutes. They were subsequently polished with 1  $\mu\text{m}$  diamond paste for 3 minutes and ultrasonically cleaned differently in the time range 3–90 minutes. The results suggest that there is a slight decrease in the nucleation density with increase in the ultrasonic cleaning duration. For example, ultrasonic cleaning for 3 minutes resulted in a nucleation density of approximately  $1.8 \times 10^8 \text{ cm}^{-2}$  and 35 minutes of cleaning gave a nucleation density of  $1.5 \times 10^8 \text{ cm}^{-2}$ . The nucleation density was similar at around  $1.4 \times 10^8 \text{ cm}^{-2}$  for an ultrasonic cleaning for 90 minutes. The results are in agreement with those reported by Bienk et al [15] who employed a similar process on silicon substrates. However, the ultrasonic cleaning reduces the nucleation density more obviously for Si substrates. This is probably because copper is a relatively soft metal which allows the residues from the polishing process to be seeded into its surface during the polishing process. Ultrasonic cleaning may not be able to remove these residues as efficiently from copper substrates than from the harder silicon substrates.

Substrate biasing is typically performed on polished materials. It would be interesting to know whether polishing the substrates with different abrasives have an effect on the overall diamond nucleation density. Table 1 shows the nucleation densities obtained with and without the biasing stage for each of the polishing materials used to pre-treat the copper substrates. The biasing stage involved the application of bias voltages of up to  $-300 \text{ V}$  for 30 minutes followed by diamond deposition for one hour under standard CVD conditions. It is evident from Table 1 that substrate biasing enhances the nucleation density in all cases investigated. The nucleation densities of the deposited diamond crystallites were calculated using SEM images of the films, taken after 60 minutes of deposition following the initial biasing stage. The highest nucleation density of  $2.75 \times 10^8 \text{ cm}^{-2}$  was obtained when biasing diamond powder polished surface. Silicon carbide polished surfaces exhibited the lowest nucleation density values. The net increase in the nucleation density with the biasing process fol-

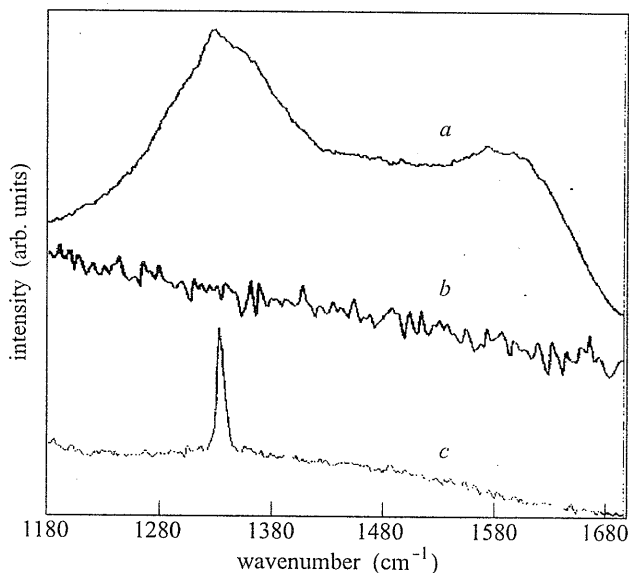
lows a sequence: diamond powder polished surface > diamond paste polished surface > alumina polished surface > silicon carbide polished surface. However, the percentage increase in the nucleation density achieved by combining both polishing and biasing pre-treatments displays a different sequence. Table 1 also shows that the percentage increase in the nucleation density is the highest with diamond paste followed by diamond powder, SiC paper and Al<sub>2</sub>O<sub>3</sub> paste. It is worth noting that the sequence of the relative increase in the nucleation density is in accordance with the surface roughness values of copper substrates polished with diamond paste, diamond powder, alumina paste and silicon carbide, as shown in Table 2. As a summary, biasing copper substrates polished with diamond powder gave the highest nucleation densities, while the biasing process was most effective on copper surfaces which were polished with 3 μm diamond paste, producing the smoothest surface. These results suggest that the biasing process is highly sensitive to both surface roughness and the residues embedded in the substrate from the polishing materials. In addition, it was noted that the substrate temperature dropped from 1115 to 1100 K once the bias was switched off. Studies have shown as expected that higher nucleation densities and deposition rates are possible when employing higher substrate temperatures [16]. Generally, at elevated substrate temperatures any species/residues, which may be present at the substrate surface will have greater energy and thus greater surface mobility to find active sites and participate in nucleation reactions.

**Table 2**

Polishing material	Surface roughness of copper substrate before the biasing stage, $R_a$ (μm)
Diamond powder	0.022
Diamond paste	0.017
Al <sub>2</sub> O <sub>3</sub> paste	0.032
SiC	0.032

Figure 2 shows Raman spectra of copper substrates (polished with 3 μm diamond powder) which were treated as follows: (a) only biased; (b) biased and then exposed to hydrogen plasma for 10 minutes; and (c) biased followed by 5 hour subsequent diamond deposition under normal CVD conditions. The biasing stage lasted for a total of 30 minutes. After the biasing stage, two major peaks were found to be present in the Raman spectra. A broad peak centred at  $\approx 1350 \text{ cm}^{-1}$  representing the *D*-band of microcrystalline graphite is evident in Fig. 2a. Furthermore, the Raman spectra reveals the presence of a broad band centred at around  $1580 \text{ cm}^{-1}$ , which is characteristic of a *G*-band of microcrystalline graphite. The spectrum does not indicate the presence of any diamond crystallites.

X-ray diffraction studies revealed that no diamond crystals were present in the carbon precursor produced after the biasing process. It was interesting to note that once the carbon precursor was exposed to hydrogen plasma for 10 minutes the *D*- and *G*-bands of microcrystalline graphite disappeared from the Raman spectra (Fig. 2*b*).



**Fig. 2.** Raman spectra of copper substrates polished with 3  $\mu\text{m}$  diamond powder

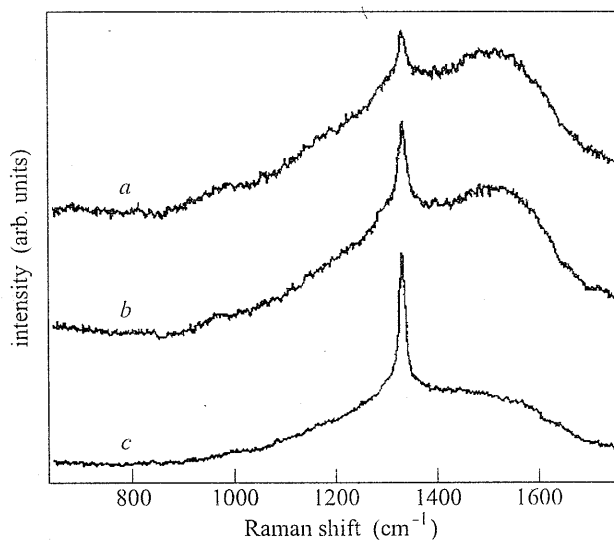
(*a*) only biased; (*b*) biased and then exposed to hydrogen plasma for 10 minutes; (*c*) biased followed by 5 hour subsequent diamond deposition under normal CVD conditions

This observation could be attributed to the etching effect of the hydrogen ions in the hydrogen plasma. This suggests that the deposited material at this stage consists of a carbon network which is etched easily by the hydrogen plasma, such as amorphous carbon and microcrystalline graphite. Gouzman and co-workers have found that the carbon precursor deposited during sample biasing maintained its stability under exposure to hydrogen plasma [17]. They found that the carbon precursor consisted of nanocrystalline diamond particles. However, in their case a silicon substrate was employed and sample biasing was conducted by means of microwave plasma-enhanced CVD. The differences in the respective studies could be due to ionisation in the deposition systems and process conditions. We found that with subsequent diamond deposition the two broad bands centred around 1350 and 1580  $\text{cm}^{-1}$  disappeared and a relatively intense diamond peak centred at around 1332  $\text{cm}^{-1}$  appeared on the Raman

spectra (Fig. 2c). This signifies the existence of a good quality diamond. Our initial findings have shown that during the biasing process the emission current is believed to play an important role in the nucleation of diamond particles on copper [18].

### 3.2. Effect of Process Parameters on Diamond Deposition

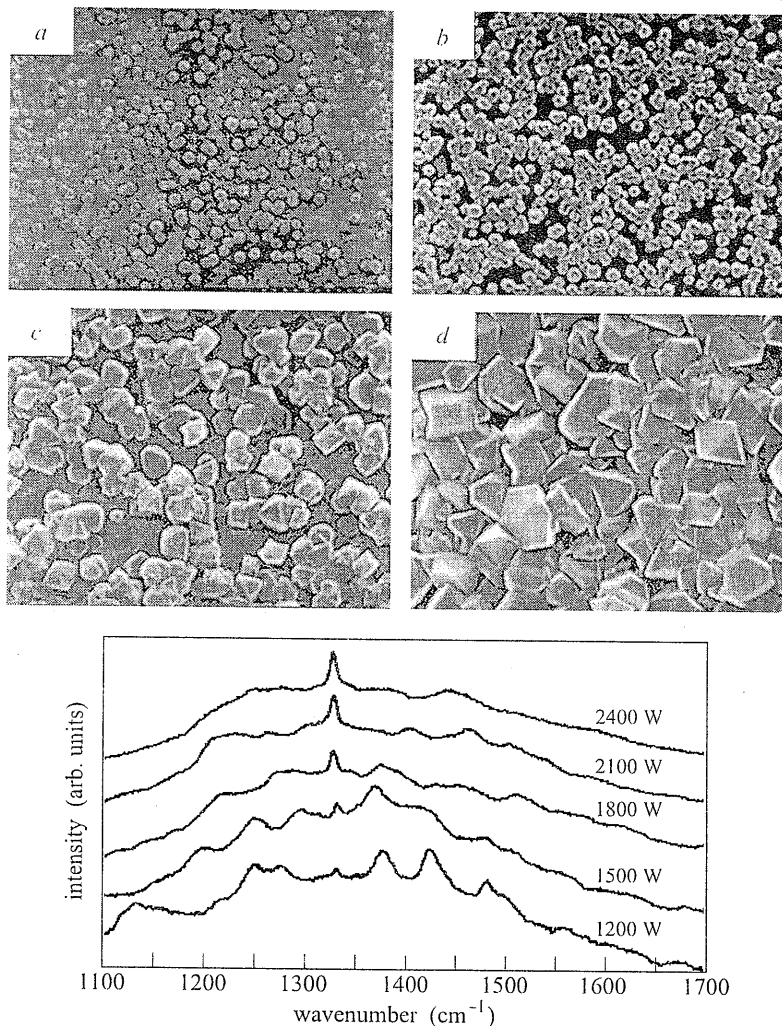
In general, the properties of the coatings deposited by CVD are highly dependent on the process parameters such as substrate temperature, reactor pressure, filament temperature, gas flow rates, methane concentration and plasma power. These parameters need to be optimised in order to produce the best coating characteristics.



**Fig. 3.** Raman spectra of three diamond films deposited on copper using HFCVD (a) 3%; (b) 2%; (c) 1% methane concentrations

Figure 3a, b and c shows the Raman spectra of three diamond films deposited using HFCVD at 3%, 2% and 1% methane concentrations, respectively. Under these growth conditions it is apparent that the quality of the diamond films decreases with increasing methane concentration as gauged from the intensity of the 1332 cm<sup>-1</sup> Raman peak. It is important to realise that the films exhibited similar thicknesses of the order of  $\approx 4\text{--}5\ \mu\text{m}$ . It is evident that as the methane concentration increases, the quality of the diamond films deteriorates, while the diamond nucleation density is found to increase. The increase in diamond nucleation density can be expected as more carbon-containing radicals are generated, whilst the etching effect of atomic hydrogen may have become

relatively smaller. Also, more non-carbon phases are a consequence of higher methane concentrations, as can be seen from the broad absorption band around  $1530\text{ cm}^{-1}$  in the Raman spectra.



**Fig. 4.** SEM images of the deposits synthesised using MPCVD (a) 1200 W; (b) 1500 W; (c) 1800 W; (d) 2400 W microwave power; (e) their Raman spectra

Figure 4 shows the SEM images of the deposits synthesised using MPCVD at microwave powers from 1200 to 2400 W (corresponding to substrate temperature 500–900 °C) and their Raman spectra. As expected the growth rate

increases from 0.2 to 1  $\mu\text{m/h}$  when the microwave power is varied from 1500 to 1800 W. There is a corresponding increase in the intensity of the diamond peak at  $1332\text{ cm}^{-1}$  with microwave power, implying increasing diamond-like character in the deposited film. When the microwave power is lower than 1500 W many amorphous components are formed, as confirmed by Raman spectroscopy analysis. This behaviour is similar to the substrate temperature affect and suggests that the influence of microwave power could be partially due to the increase in the substrate temperature as the power levels are increased. The increase in microwave power also has two other accompanying effects. Firstly, the gas temperature increases as a result of redistribution of microwave energy transferred by the electrons. Secondly, the plasma status (i. e. the degree of dissociation and ionisation of hydrogen and methane gases, electron temperature, concentration of carbon-containing radicals, etc) changes with microwave power. Figure 5 shows the grain growth rate at different microwave power or substrate temperature. At microwave power lower than 1500 W, the grain growth rate is relatively low, but a rapid increase occurs at 1800 W. However, the increase slows down after a power level of 2400 W. This effect could be related to the low substrate temperature which can result in insufficient hydrogen abstraction. At the midpoint ( $\approx 1800\text{ W}$  power and  $700^\circ\text{C}$ ) the hydrogen abstraction starts to increase proportionally. However, when the substrate temperature becomes too high (i. e.  $\geq 900^\circ\text{C}$ ), the hydrogen abstraction reaches saturation. Kim et al [19] have demonstrated that the growth limitation is dominated by hydrogen abstraction only at substrate temperatures lower than  $1000^\circ\text{C}$ .

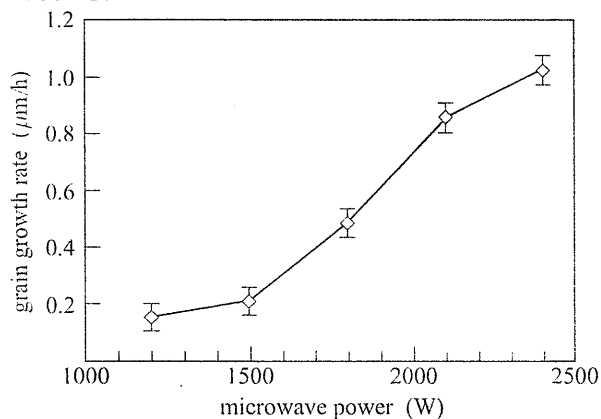


Fig. 5. Effect of microwave power or substrate temperature on grain growth rate

### 3.3. Evaluation of Diamond Coating Adhesion

One way of obtaining adherent diamond coatings on copper and steel substrates is to employ interlayer materials. An interlayer material must form a

strong carbide bond so that adhesion between diamond and copper can occur readily. Furthermore, it must possess high mutual diffusion with copper. The relative carbide-bond strengths and the diffusibilities [20, 21] of some possible interlayer materials are shown in Table 3. Silicon is the most widely used substrate material for the deposition of diamond by CVD due to its potential applications in microelectronics. However, its rupture toughness is relatively low, making it not suitable for an interlayer material. It can be seen that Cr too forms a relatively strong carbide bond and it also has reasonable diffusibility in copper substrates. Therefore, Cr can also be a suitable interlayer material for improving the adhesion between diamond and copper. The carbon diffusion in Cr is also relatively low compared to other metals, also shown in Table 3. This means that Cr does not allow high rate of carbon diffusion during diamond deposition and therefore, is expected to improve the adhesion between diamond and copper considerably. It is also worth noting that Ti has an impressive diffusibility in carbon. The Ti-C bond is known to be as strong as Si-C. Therefore, titanium is another potential interlayer material which can provide better diamond coating adhesion on metals such as copper and steel.

Table 3

Diffusibility in carbon		Carbide bond strength		Diffusibility in copper	
Ti	↑ increasing diffusibility	SiC	↑ increasing bond strength	Si	↑ increasing diffusibility
Si		CrC		Cr	
Cr		WC		W	
W ≈ Mo		MoC		Mo	

### 3.3.1. Adhesion Analysis by Micro-Raman Spectroscopy

Figure 6 shows a schematic diagram of a steel impresser being applied to the diamond coating (deposited using HFCVD) on the copper substrate with the Cr interlayer material. It was noted that after removing the load, the resultant diamond film did not crack. However, it was observed that a white zone appeared directly under the impresser. Raman spectroscopy has been used to obtain a better understanding of the coating adhesion as it has the advantage of being non-destructive. This was carried out by monitoring the change in the Raman peak wavenumber. Prior to diamond film impression, it was observed that the diamond peak appeared at a wavenumber of about  $1334 \text{ cm}^{-1}$  and this was found to be constant all over the sample. After the impression, the diamond Raman peak shifts to different wavenumbers (in between  $1332$  and  $1334 \text{ cm}^{-1}$ ) in the area around the impression, as shown in Figs 6 and 7a. In the white zone (region 1) the Raman peak locates at  $\approx 1332 \text{ cm}^{-1}$  and in region 2, the Raman peak appears at wavenumbers between those of region 1 and 3. It is known that the Raman shift is proportional to the biaxial stress in the film. The

shift in the diamond Raman peak to higher wavenumbers has been attributed to a compressive stress, which is caused mainly by a mismatch in the thermal expansion coefficients of the diamond and the copper [22].

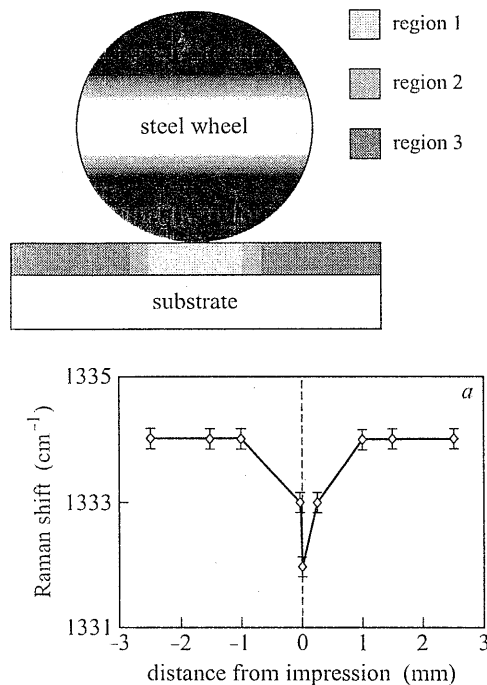


Fig. 6. A steel impresser being applied to a diamond coating on a copper substrate with a Cr interlayer material

Fig. 7. (a) Variation in the Raman diamond peak value around the impression region on diamond/Cr/Cu sample  
(b) Shift in the Raman diamond peak around the impression centre on diamond/Ti/Cu sample

Figure 7 indicates that before the impression test the films adhere to the substrate and therefore are subjected to an uniform compressive stress. After the test, the film in region 1 becomes almost stress free since the load stress is larger than the fracture strength of the film/substrate interface and consequently the film detaches from the substrate and no longer possesses adhesion. In region 2 the load stress is comparable to the fracture strength and the film detaches partly from the substrate and the adhesion deteriorates. In region 3 the load stress is so small that it does not affect the film adhesion status. The adhesion or detachment degree is indicative from the diamond Raman peak shift. A higher Raman shift indicates that the coating can stand a larger residual stress and therefore implies a better adhesion. This result seems in contradiction with the traditional teaching that a greater stress usually results in poor adhesion.

However, it should be noted that in the present case, the value of residual stress evaluated from the diamond Raman line shift is much smaller than the thermal stress [23]. Figure 7b shows the shift in the Raman diamond peak around the vicinity of the impression centre performed on diamond coating on copper using a titanium interlayer. It is worth noting that the coatings on copper using a titanium interlayer have been deposited using MPCVD system and not HFCVD. It is evident that the shift in the Raman diamond peak away from the  $1332\text{ cm}^{-1}$  value is the greatest at positions furthest away from the impression centre. At the point where the peak position is at  $1332\text{ cm}^{-1}$  the film is stress free and behaves as a free standing diamond film. However, a comparison of diamond coating adhesion with respect to the film stress is not possible by the Raman technique, this being the main disadvantage of the particular method.

### 3.3.2. Pull-off Test

Diamond coatings deposited by both HFCVD and MPCVD on copper (coated with Ti and Cr) were tested for adhesion using the pull-off test method. The result reveals that the debonding occurs between the diamond film and the epoxy adhesive. Figure 8 shows a typical test result obtained after the pull-off test. This suggests that the adhesion of the diamond film to the copper substrate is stronger than the peel strength of the epoxy. Therefore, with respect to the pull-off tests, we conclude that both Cr and Ti interlayers are effective in obtaining adequately adherent diamond coatings on copper substrates and the coating adhesion is better than the value of  $\approx 14\text{ MPa}$ . As a result of the glue strength limitations the critical detaching force of the coating was not assessed by the pull-off method.

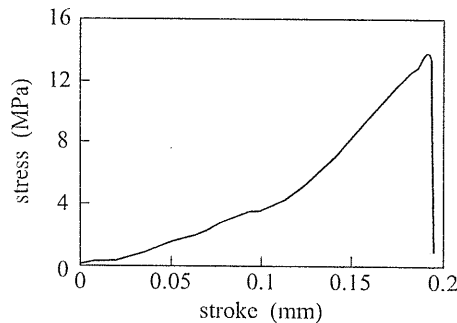


Fig. 8. A typical test result obtained after the pull-off test

### 3.3.3. Scratch Test

Scratch tests were found to be more qualitative than the pull-off tests. A critical load value was extracted from the scratch tests, which indicated a load at which the coating adhesion failed. In this investigation, four polycrystalline

films were deposited on copper/chromium surface using HFCVD. Prior to diamond deposition the samples were bias pre-treated for 0, 5, 10 and 15 minutes, respectively. Figure 9 shows the graph relating critical load to bias time, as obtained from the scratch test results. The bias treated samples exhibited a much higher critical load than the non-biased samples, indicating a significant increase in the coating adhesion. There are two ways to explain this trend. Firstly, the nucleation density increases with bias time [24], which provides stronger mechanical interlock and consequently improves the coating adhesion. Secondly, longer nucleation duration on the non-bias sample leads to greater carbon diffusion in the Cr/Cu substrate and therefore reduces the coating adhesion. Therefore, the scratch tests are effective in qualitative comparison of the coating adhesion. The main problem encountered with the scratch tests was the damage inflicted to the diamond tip during horizontal scratching motion.

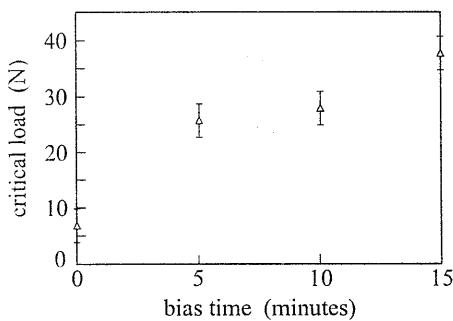


Fig. 9. Graph relating critical load to bias time, as obtained from the scratch test results

#### 3.3.4. Indentation/Acoustic Emission Method

From above discussion, we can see that conventional adhesion tests encounter some problems when evaluating the diamond coatings. A new method has been developed recently, which combines the indentation tests and acoustic emission during loading [25]. With this method we compared the adhesion of diamond coatings on bulk Cr and Ti substrates and on steel substrate with a Ti interlayer.

Polycrystalline films of diamond were deposited on pure Ti and Cr substrates using MPCVD system. The coatings were tested for adhesion using the modified indentation method, which combined indentations with acoustic emissions. Indentations were performed at 180 N load on the coated samples. The resultant indented surfaces were examined under an optical microscope, which was connected to a computerised camera. Figure 10 shows the microscopic images of the indented diamond coatings on chromium (a) and titanium (b) substrates. It is worth noting that the magnification of these images is  $50\times$ . It is clearly visible that the indentation has had a detrimental effect on the diamond coating on the chromium substrate. The coating had delaminated from the substrate around the indentation mark (Fig. 10a). The lighter region visible

on the microscopic image is the bare chromium substrate. At the centre of the indentation mark the diamond film deforms with the substrate and remains on the chromium, whereas, around the indentation mark the coating peels off leaving behind just the substrate. On the contrary, the indentation test on the diamond/titanium surface produces different result, where the diamond film does not delaminate from the Ti substrate. However, a small circular white region can be found on the image around the indentation mark. This is the region where the film has slightly detached from the substrate, but the detachment is localised. Therefore, diamond adhesion is better on Ti than it is on Cr.

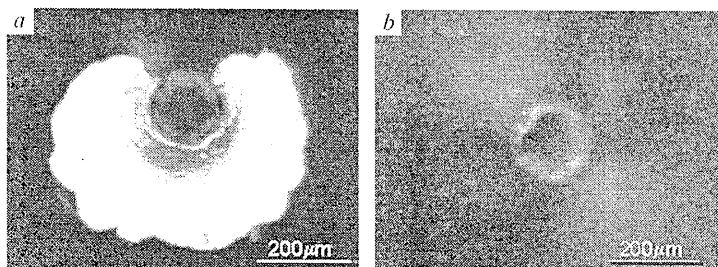


Fig. 10. Microscopic images of the indented diamond coatings on chromium (a) and titanium (b) substrates

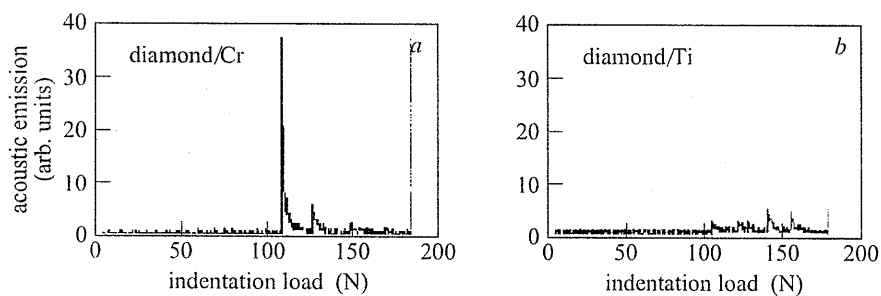
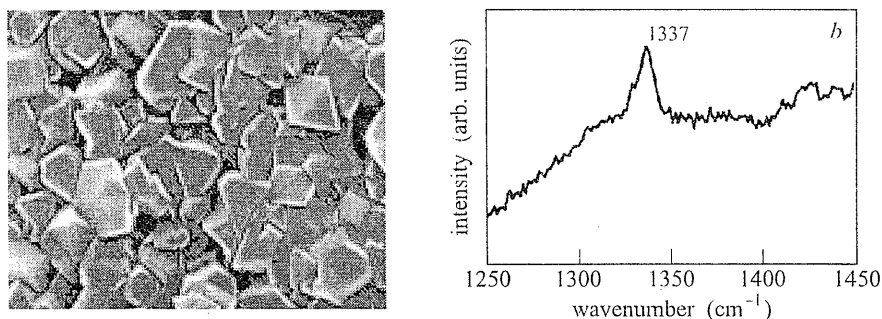


Fig. 11. Acoustic emission spectra obtained from diamond coatings on Cr (a) and Ti (b) during indentation at 180 N load

As a further confirmation of the above finding, acoustic emissions during the indentations were recorded automatically during loading in order to compare the coating adhesion. Figure 11 shows acoustic emission spectra obtained from diamond coatings on Cr (a) and Ti (b) during indentation at 180 N load. The first feature in the spectra appeared at a load approximately 105 N, which was considered as the critical load that caused the film to either crack or delaminate from the substrate. However, we have found that for the diamond coating on chromium a much more intense acoustic emission peak at  $\approx 105$  N is evident. This is because the film starts to break off the substrate, thus producing higher

acoustic emission signals. Further indentation tests indeed showed that the film peeled off the substrate once the indentation load was greater than 105 N. However, AE signals for the diamond/titanium sample were much less intense. This may be due to the fact that during indentation the diamond coating deforms locally. Once reaching a critical load, the film starts to crack locally, emitting low intensity AE signals. However, the film contains itself and continues to remain attached to the titanium substrate. The AE spectra have further strengthened our finding that diamond bonds more strongly to titanium than it does to chromium and therefore titanium is a more suitable material for use as an intermediate layer.

Direct diamond deposition on stainless steel is feasible, however, the nucleation density and the adhesion is poor [8]. Titanium has been used as an interlayer to enhance diamond adhesion on steel. Figure 12 shows the SEM image and Raman spectra of a diamond film grown at 2100 W for 3 hours on the steel substrate with a 2  $\mu\text{m}$  thick Ti interlayer. It is evident that the diamond Raman peak shifts to  $1337\text{ cm}^{-1}$ , indicating that a compressive stress exists in the diamond film. However, the resultant diamond coating can accommodate the stress without having to delaminate from the steel substrate.



**Fig. 12.** SEM image and Raman spectra of a diamond film grown at 2100 W for 3 h on the steel substrate with a 2  $\mu\text{m}$  thick Ti interlayer

The coating adhesion on the steel substrate was also analysed using the previously described modified indentation test method. It was found that some local delamination occurred at a load of 10 N. However, the film remained on the substrate until a load of 55 N, at which point the film broke off. We therefore conclude that adherent diamond coatings on steel can be achieved with a Ti interlayer, but the coating adhesion deteriorates when compared to the films grown directly on pure Ti, which shows a critical indentation load at around 105 N. The reason is probably due to the mutual diffusion of carbon and iron through the thin Ti interlayer.

#### 4. Conclusion

Thin polycrystalline films of diamond have been deposited using HFCVD and MPCVD processes. The diamond nucleation density has been found to be sensitive to the polishing material and the particle size of the abrasive. Smaller particle size in the polishing material and longer polishing times result in improved nucleation densities. Substrate biasing has been combined with polishing to further increase diamond nucleation density. It has been observed that by amalgamating the two pre-treatment methods there is an enhancement in the overall nucleation density with all the polishing materials used. The biasing process produces *D*- and *G*-bands of graphite which are readily etched away when exposed to a hydrogen plasma. Methane gas concentration was found to be optimum at 1%. Increase in the microwave power resulted in enhanced growth rates.

Both Ti and Cr have been employed as interlayer materials to improve the adherence between copper/steel and diamond films. Conventional adhesion test methods, such as pull-off and scratch tests, encounter some problems when evaluating the diamond coatings. An indentation test combined with acoustic emissions is employed to compare qualitatively the coating adhesion. This new method reveals that diamond bonds more strongly to Ti than it does to Cr. Employing Ti as an intermediate layer improves both the density and the adhesion of the resultant diamond films on steel substrates. However, it is observed that diamond bonds more strongly on bulk Ti than it does to thin film Ti. This is due to the mutual diffusion of carbon and iron through the relatively thin Ti interlayer as compared to the bulk Ti substrate.

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#### References

1. N. Ali, W. Ahmed, I. Hassan and C. Rego. *Surface Engineering* **14**(4) (1998) 292-294.
2. N. Ali, W. Ahmed and I. Hassan. *Materials World* **6**(6) (1998) 348-350.
3. W. Ahmed, C. Rego, A. Afzal, N. Ali and I. Hassan. *Vacuum* **55** (1999) 1-5.
4. N. Ali, Q. Fan, W. Ahmed, I. Hassan, C. Rego and I. O'Hare. *Thin Solid Films* **355/356** (1999) 162-166.
5. V. Ralchenko, E. Obraztsova, K. Korotoushenko, S. Pimenov, A. Smolin, V. Pereverzev, Y. Lakhokin and E. Loubnin. In: *Proceedings of the Applied Diamond Conference 1995*, 21-24 Aug 1995, Gaithersburg, MD, USA, pp 635-8.
6. J. Narayan, V. Godbole, G. Matera and R. Singh. *J. Appl. Phys.* **71**(2) (1992) 966.

7. S. Bull and D. Rickerby. In: *Advanced Surface Coatings: A Handbook of Surface Engineering*, D. Rickerby and A. Matthews (Eds), Chapman and Hall Inc., New York 1991, p. 315.
8. N. Ali, W. Ahmed and Q. Fan. *Surface Engineering* **16**(5) (2000) 422.
9. R. Bauer, N. Sbrockey and W. Brower. *J. Mater. Res.* **8**(11) (1992) 2858.
10. G. Popovici and M. Prelas. *Physica Statistica Solidi A* **132**(2) (1992) 233.
11. T. Hartnett, R. Miller, D. Montanari, C. Willingham and R. Tustison. *J. Vac. Sci. Technol. A* **8** (1990) 2129.
12. Q. Fan, E. Pereira and J. Gracio. *J. Mater. Sci.* **33** (1998) 3.
13. H. Maeda, S. Masuda, K. Kusakabe and S. Morooka. *J. Crys. Growth* **121**(3) (1992) 507.
14. M. Yoshikawa, Y. Kaneko, C. F. Yang and H. Tokura. *J. Japan Soc. Precision Eng.* **55**(1) (1989) 155.
15. E. Bienk and S. Eskildsen. *Diamond Relat. Mater.* **2** (1993) 432.
16. Y. Hayashi, W. Drawl and R. Messier. *Jpn. J. Appl. Phys.* **31** (1992) L194.
17. I. Gouzman, B. Fiskeer, Y. Avilgal, R. Kalish and A. Hoffman. *Diamond Relat. Mater.* **6** (1997) 526.
18. N. Ali, W. Ahmed, Q. Fan, I. O'Hare and C. Rego. *J. Mater. Sci. & Technology.* **7**(3) (1999) 15-24.
19. J. Kim, M. Kim, S. Park and J. Lee. *J. Appl. Phys.* **67** (1990) 3354.
20. Q. Fan, A. Fernandes, E. Pereira and J. Gracio. *Vacuum* **52** (1999) 193.
21. *Handbook of Chemistry and Physics*, 57th edn, R. Weast (Ed), CRC Press Inc., New York 1976, pp F-63-219.
22. W. Banholzer and R. Kehl. *Surface and Coat. Technol.* **47** (1991) 57.
23. Q. Fan, J. Gracio, E. Pereira. *J. Appl. Phys.* **84** (1998) 3155.
24. N. Ali, W. Ahmed, Q. Fan and C. Rego. *Diamond and Related Materials* **9** (2000) 1465.
25. Q. Fan, J. Gracio and E. Pereira. *J. Appl. Phys.* **86** (1999) 5509.