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A REVIEW ON THE MORPHOLOGY OF DIAMOND THIN FILM COATING ON VARIOUS TYPES OF SUBSTRATE MATERIALS

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ABSTRACT

Diamond coatings are employed to yield significant benefits in applications such as for cutting tools, optical lenses, biomedical components, microelectronics, engineering, and thermal management systems. However, several process parameters must be studied to get optimum coating and eliminated disadvantages results. Chemical Vapor Deposition (CVD) technique is commonly used for diamond coating. This paper reports on investigations in the last few years on CVD process and problems associated with it such as gas mixture, substrate materials and coating adhesion. Emphasis is given to achieve process optimization by selection of substrate material and process parameter is controlled to obtain high quality morphology of thin film diamond coating. Some materials are suitable substrate for diamond nucleation and growth. Increase in substrate temperature and %CH_4 *in* H_2 *in gas mixture can cause an increase in the nucleation and crystal growth rate and grain size, but the diamond quality will be reduced. Whereas increase in reactor pressure will decrease crystal growth but the diamond quality will be improved. Structure and morphology were investigated by Scanning Electron Microscopy (SEM) and diamond thin film quality by Raman Spectra.*

Keywords: *Thin film coating; CVD; Cutting Tool; Raman Spectra.*

1.0 INTRODUCTION

Diamond is a unique engineering material, due to its superior combination of physical, optical and chemical properties [1]. Diamond is far the hardest material known and thus it is possible to take advantage of these properties in many engineering applications for which high hardness, high resistance to corrosion and erosion is required. CVD Diamond is used extensively in cutting tool.

Raman spectra are more sensitive to the lengths, strengths, and arrangement of bonds in a material than to chemical composition. Raman spectra of crystals likewise reflect the details of defects and disorder rather than trace impurities and related chemical imperfections. The laser-optical Raman technique can determine with great confidence the atomic bonding states of the carbon atoms (sp^2 for graphite or sp^3 for diamond) from their different vibrational modes. Raman spectra result from the inelastic scattering of optical photons by lattice vibration phonons. [2].

Badzian et al [3] reported that the temperature, chamber pressure, ratio of CH_4/H_2+CH_4 in the gas mixture and gas flow rate were the main parameters affecting growth rate and quality.

The objective of this paper is to review the parameters namely substrate material, substrate temperature, gas mixture, and reactor pressure on morphology and quality of diamond coating on various types of materials based on previous experiments from other researchers. The analysis of the microstructure and morphology by using SEM was also reported. Raman Spectra determined the quality of diamond.

2.0 EFFECT OF SUBSTRATE MATERIAL

Gordana S. Ristic et al [4] investigated the effect of substrate material on CVD diamond coating properties. The experiment involved different types of materials i.e. Copper (Cu), Widia Metal (WC – Co), Molybdenum (Mo), and Silicon (Si). Hot filament CVD was used in the deposition process with the filament temperature was kept at 2100 – 2200°C, gas mixture of 1% CH_4 in H_2, deposition time was around 30 h. The total gas pressure was 30 mbar and gas mixture flow $40cm^3\ min^{-1}$. This had an effect on the thickness of the deposited layer. The structure and morphology of the facet was investigated by SEM as shown in Figure 1 and morphology defects as shown in Figure 2. The quality and properties of diamond coating were determined by Raman Spectra as illustrated in Figure 3.

Figure 1 shows the effect of substrate material on the structure of the diamond. Figure 1(a) provides evidence of characteristic {111} with triangular-faceted morphology, Fig. 1(b) clearly shows secondary nucleation has occurred. The top view of the surface coating onto Mo shows the triangular-shape morphology (Figure 1(c)), and Figure 1(d) shows mainly non-crystalline phase when similar diamond coating was deposited on silicon. The disadvantages each material as substrate is shown Figure 2. In Cu substrate for instance, defects such as cracks were observed in the coating (Figure 2(a)), other material such as WC – Co, Mo, and Si show no cracks but only native fracture of the coating.

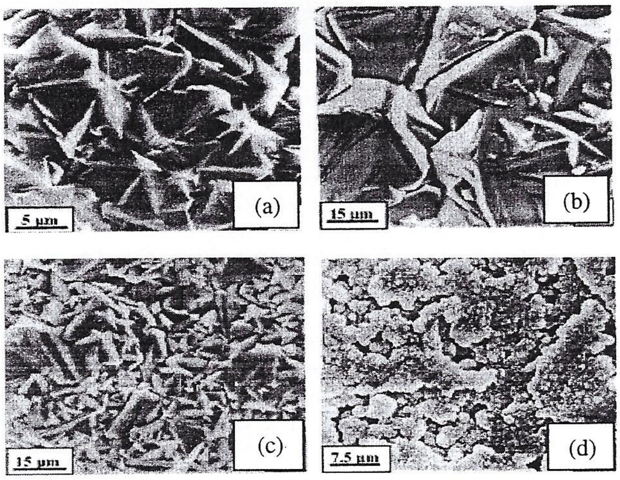


Figure 1: SEM micrographs show surface morphology of diamond coating with similar deposition parameters but on different substrate materials (a) Cu; (b) WC-Co; (c) Mo; (d) Si [4]

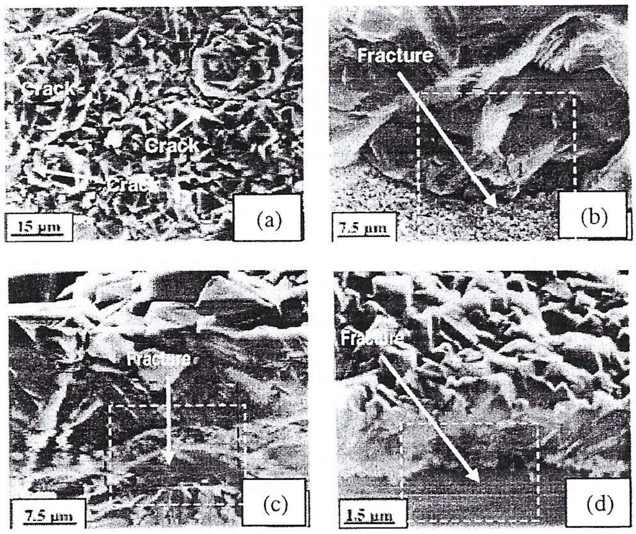


Figure 2: SEM micrograph show surface morphology defect of diamond coating with similar deposition parameters but on different substrate materials (a) Cu; (b) WC-Co; (c) Mo; (d) Si [4]

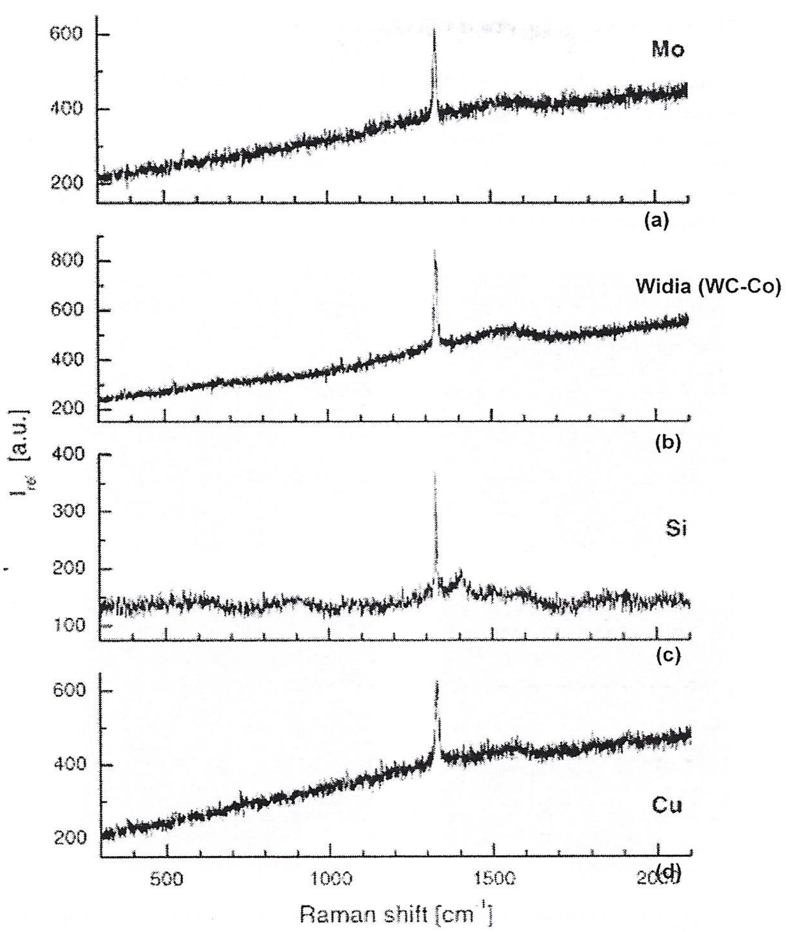


Figure 3: Raman spectra of diamond coating deposited on different substrate materials (a) Mo, (b) Widia (WC – Co), (c) Si, and (d) Cu [4].

The atomic bonding states of the carbon atoms (sp^2 for graphite or sp^3 for diamond) were investigated by using Raman Spectra technique. Figure 3 shows the distinct peak at around 1332.5 cm^{-1} stems from diamond. Low background of amorphous carbon between 1100 and 1700 cm^{-1}, with a hump centered at about 1550 cm^{-1}, can be seen for good-quality diamond coatings. Strong luminescence is observed from the diamond coating–metal substrate (Cu, Mo, WC-Co) system, but not from the diamond coating on Si substrate system.

3.0 EFFECT OF SUBSTRATE TEMPERATURE AND GAS MIXTURE

Diamond surface morphology not only depends on substrate material but also other parameters i.e. surface temperature, gas flow mixture etc. It has been reported that the substrate temperature and gas mixture have an effect on crystal growth and coating surface morphology [5]. Molybdenum was used as the substrate material. Figure 4 shows morphology of the coating when varying substrate temperature and CH_4/H_2 ratio.

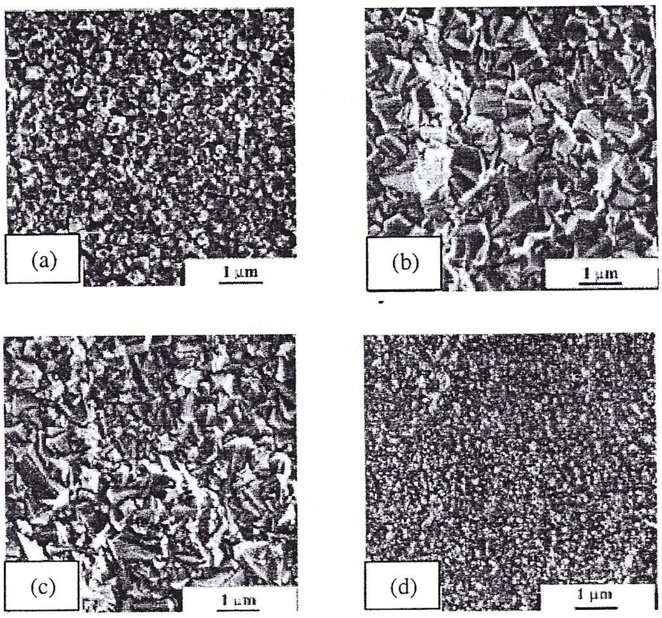
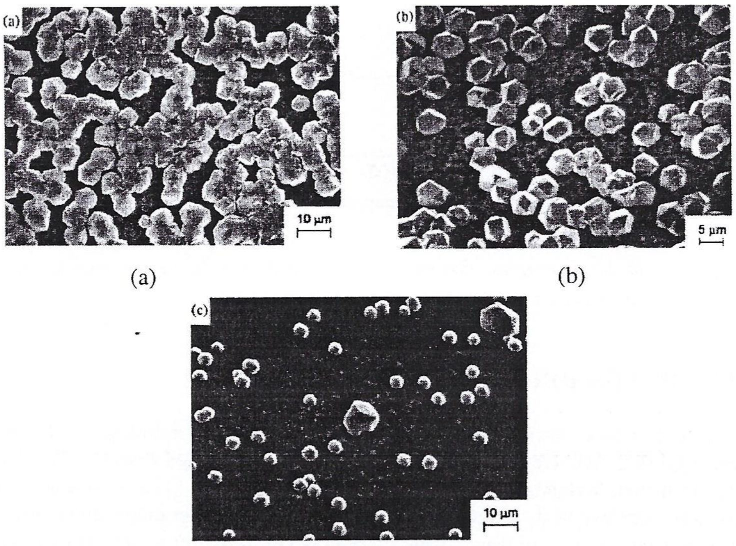


Figure 4: SEM micrograph of the diamond film surfaces obtained at varying deposition condition i.e. substrate temperature and CH4/H_2 ratio (a) 475°C, 0.5% vol. CH_4 in H_2 (b) 650°C, 0.5% vol. CH_4 in H_2 (c) 750°C, 0.5% vol. CH_4 in H_2 (d) 750°C, 4% vol. CH_4 in H_2 [5]

Figure 4(a) and 4(b) show the surface morphologies of the grown diamond layers deposited at different substrate temperatures with similar CH_4/H_2 ratio. The grain size at 475°C substrate temperature is smaller than the grain size at temperature 650°C. The effect of gas mixture concentration CH_4/H_2 is shown in Fig. 4(c) and 4(d). Microcrystalline structures are formed (Figure 4c) when CH_4/H_2 ratio of 0.5% is used, whereas for 4.0% ratio, only nanocrystalline structures are observed (Figure 4d).

4.0 EFFECT OF REACTOR PRESSURE

The reactor pressure has the strongest influence on nucleation in Microwave Plasma Assisted CVD (MPACVD) process, followed by temperature and % CH_4 concentration. Mallika and Komanduri [6] investigated the influence of reactor pressure in substrate material by using MPCVD, gas mixture 1% CH_4 in H_2 and the results are shown in Figure (5) and Figure (6).



(a) (b)

(c)

Figure 5: SEM micrographs show the effect of diamond nucleation and substrate (Si_3N_4) etching with chamber pressure. (a) 20 torr (b) 40 torr. (c) 60 torr [6]

Figure 5 shows structure of diamond coating at different pressures namely 20, 40, and 60 torr with 1% CH_4 concentration. As can be seen in Figure 5, the chamber pressure affects the size and density of diamond nucleation. Another important observation can be made from Raman Spectra as shown in Figure 6 that different of relative intensity with different pressure chamber.

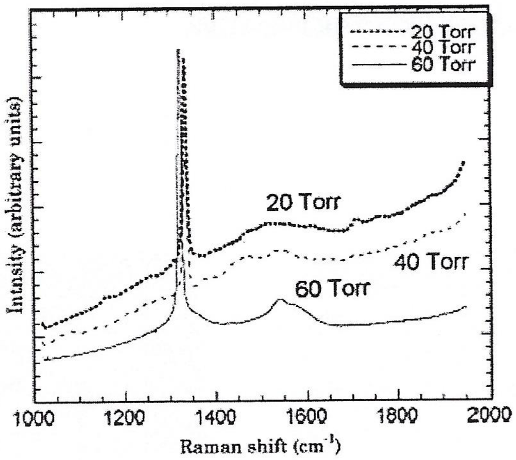


Figure 6: Raman spectra shows diamond and non-diamond peaks on Si_3N_4 substrates at different chamber pressures [6]

5.0 DISCUSSION

Figure 1 shows variation of surface diamond coating morphology with substrate material (Cu, WC-Co, Mo, and Si). Diamond was deposited onto Cu, WC-Mo and Mo indicated formation of well faceted diamond crystal {111}. In single crystal Si as substrate material, it was found that an extremely inhomogeneous, very thin, fine-grained coating of mixed morphology and region with a large amount of non-crystalline phase was obtained. Diamond deposition on Cu is characterized by the fact that Cu does not form any chemical compound with gaseous precursor of diamond. This gives rise to poor adhesion of diamond coating on Cu, as forces of chemical bonding on the interface do not exist. Cu and diamond have different Coefficient of Thermal Expansion (Cu $\approx 17 \times 10^{-6}$ K^{-1}, diamond $\approx 1 \times 10^{-6}$ K^{-1}) [7]. Hence, decreasing the temperature at the end of experiment caused sporadic cracking of the film and irregular, random delamination from the substrate as shown in Figure 2(a). Defects occurred in other substrates are relatively similar as shown in Figure 2(b) to 2(d). Native fracture coating is the result of the vertical growth of a particular crystal throughout the coating.

SEM micrograph in Figure 1(b) shows diamond coating on WC–Co substrate by using HFCVD. The diamond film nucleates and grows without any problem onto the WC–Co substrate, provided Co has been removed from the surface, for example, by chemical etching, plasma etching or by depositing a buffer layer. Because of the high solubility and diffusivity of carbon in Co, the latter acts as a carbon sink (with a formation of solid solution), that promotes the formation of non-diamond carbon (graphite [8] or soot [9]) and thus delays the onset of diamond nucleation. Cobalt in WC–Co substrate also increases the coefficient of thermal expansion in comparison with pure WC (without Co binder), which results in increasing of thermal (compressive) stress between the substrate and the diamond coating, and give rise to poor adhesion [10]. For the Mo substrate, diamond growth is quite significant; any special pretreatment (mechanical, chemical, physical) is not required for diamond growth on Mo. Seeding the substrate with diamond particles (i.e. nuclei for diamond growth) is not necessary. The adhesion of the diamond film on the Mo substrate is very good. In Si substrate (Figure 1(d)) the evidence shows crystal structure with no facet and ball-like structure known as cauliflower structure.

Cappelli et al. [11] studied the HFCVD deposition conditions of diamond on different tool substrate materials: cer-met (WC-Co); ceramics (SiAlON, Al_2O_3 + TiC) and whiskers reinforced ceramics (Al_2O_3 + Si and ZrO_2). The diamond paste polishing caused no significant difference in chemical composition. Whereas nitric acid etching (HNO_3/H_2O) and H_2 plasma treatment at 800°C, chamber pressure 7 torr for 1 hour resulted to be most effective in cobalt removing from the WC-Co surface (Co<1%). However, the $HNO_3/HF/H_2O$ and Murakami's reagent + HNO_3 allowed not only an adequate cobalt etching but also a surface chemical reduction and a remarkable morphological modification. Sun et al [12] reported that H_2O_2 is effective to remove Co content. All substrate materials used are good substrates for crystalline diamond nucleation and growth. However, there is problem in adhesion which is caused by the mismatch of coefficient of thermal expansion ($Al_2O_3 \approx 7.1 \times 10^{-6}. K^{-1}$, $TiC \approx 7.2 \times 10^{-6}. K^{-1}$ and $TiN \approx 8.1 \times 10^{-6}. K^{-1}$). The SiAlON substrate is the most suitable substrate for diamond deposition, owing to their ceramic nature and very similar thermal coefficient of expansion ($SiAlON \approx 3 \times 10^{-6}. K^{-1}$).

Substrate temperature and % of CH_4 concentration are found to be the most crucial parameters that dictate the overall growth rate as well as the quality of the diamond films. Zhu et al [10] reported that substrate temperature and the % CH_4 concentration affect the morphology and the growth rate of the diamond films when deposited on Si. Increase in % CH_4 concentration was found to increase the growth rate but at the expense of the quality. This result in the diamond coatings became more defective and contained graphitic inclusions. They found that the chamber pressure has a minimal effect on the morphological development.

The distinct peak at around 1332.5 cm^{-1} stems from diamond. Low background of amorphous carbon between 1100 and 1700 cm^{-1}, with a hump centered at about 1550 cm^{-1}, can be seen for good quality diamond coatings. Increasing content of amorphous phases gives rise to additional maxima. Strong luminescence is observed from the diamond coating–metal substrate (Cu, Mo, WC-Co) system, dissimilarly from the diamond coating Si substrate system (Figure 3).

Buijnsters et al. [5] reported the micro-Raman spectra of the diamond layers vary with substrate temperature and gas mixture. In constant gas mixture (CH_4/H_2 = 0.5%) the maximum diamond peak intensity is found for the films grown at 650°C. The peak position is shifted from 1333.0 cm^{-1} for the films grown at 475°C to 1336.5 cm^{-1} for those deposited at 850°C. For temperatures less than 650°C a low intensity band at about 1130 cm^{-1} is observed as well. This is commonly attributed to nanocrystalline diamond. The constant temperature 750°C with restriction of varying methane concentrations the quality of the deposited layers is decreasing with increasing methane concentration. The diamond peak intensity drastically decrease and become fully dominated by the broad D-band of graphitic carbon (centered at ~1360 cm^{-1}) when the film grown at CH_4/H_2 = 4%. For all samples grown at $CH_4/H_2 \geq 1.0\%$, the amorphous carbon band (~1500cm^{-1}), G-band of graphite (~1580 cm^{-1}) and 1150 cm^{-1} band are clearly distinguished. No significant change in the diamond peak position (~1336 cm^{-1}) is observed with respect to the applied methane concentration. Film failure upon indenting and scratching is also found to decrease when increasing the methane concentration in the CVD gas mixture.

Figure 5 shows uniform nucleation of diamond on Si_3N_4 substrate surface at a chamber pressure 20 torr, moderate nucleation of diamond due to slight etching of Si_3N_4 substrate by the plasma species at a chamber pressure of 40 torr, sparse nucleation of diamond due to pronounced etching of Si_3N_4 substrate surface by the plasma species at a chamber pressure of 60 torr. Figure 6 shows the relative intensity of the non-diamond to the crystalline diamond, which decreases with increase in pressure. Raman spectra of the diamond deposited at 60 torr (7.95 kPa) contain almost none or very little non-diamond carbon.

Sharda and Misra [13] explained that at higher pressure the mean free path between the electrons and the molecules decreases. This results in an increase in the collision frequency. Also, the number of electrons in the plasma discharge increases with increase in pressure. Both factors get multiplied and enhance the production rate of the atomic hydrogen. This, in turn, leads to a reduction in the non-diamond content at high pressures.

Mallika and Komanduri [6] investigated the optimum parameters of diamond coating on Si_3N_4 using MPACVD. The reactor pressure to have the strongest influence on the nucleation followed by the substrate temperature and % CH_4 concentration. Microwave power was found to have minimum influence. Substrate temperature and % CH_4 concentration were found to be the most crucial parameters dictating the overall growth rate as well as the quality of the diamond films. The optimum deposition conditions for producing good quality diamond coatings in a chamber pressure of ~20 torr (2.65 kPa); a microwave power of ~1000 W; a CH_4 concentration of 0.5–1%; and a substrate temperature in the range of 850–900°C. Higher microwave power was found to increase the intensity of the crystalline diamond and decrease in the non-diamond peak intensity.

6.0 CONCLUSIONS

The following conclusions can be drawn from the above discussion;

1. Co removal is very important to obtain a good diamond nucleation on WC-Co. Etching using $HNO_3/HF/H_2O$, Murakami's reagent and H_2O_2 are effective to remove cobalt content.
2. Some materials are good candidate as substrate materials for diamond nucleation and growth. However, there is a mismatch of coefficient of thermal expansion that caused poor adhesion.

3. Increasing substrate temperature and $\%CH_4$ in H_2 in gas mixture increases the nucleation and crystal growth rate and grain size but will result in poor diamond quality.
4. Increasing reactor pressure decreases crystal growth but will result in better diamond quality. Based on the μ-Raman spectroscopy, the relative intensity of the non-diamond to the crystalline phase decreases with increase in the reactor pressure.

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