MORPHOLOGICAL CHARACTERIZATION OF COMBUSTION DEPOSITED DIAMOND CRYSTALS AND FILMS

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(Received: June 28, 2001 – Accepted in Revised Form: May 15, 2002)

Abstract Single crystals and polycrystalline diamond films of several thicknesses were deposited using oxygen/acetylene combustion flame technique. The substrate used was pure polycrystalline molybdenum subjected to mechanical polishing. Quality and microstructural characteristic of diamond produced were investigated using X-Ray diffraction, Raman Spectroscopy and Scanning and Transmission Electron Microscopy. Results obtained revealed that a good quality single and polycrystalline diamond could be produced. However, a combination of various defects such as twins, dislocations and stacking faults are always present.

Key Words Morphology, Diamond, Diamond-Like Carbon (DLC), Combustion Flame Technique, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD), Raman Spectroscopy

چکیده با استفاده از شعله حاصل از احتراق مخلوط اکسیژن – استیلن تک کریستالهای الماس و پوششهای الماسی پلی کریستال با ضخامتهای مختلف رسوب داده شدند. زیرلایه مورد استفاده مولیبدن پلی کریستال بوده که توسط پولیش مکانیکی آماده سازی شده بود. کیفیت و ویژگیهای ساختاری الماس تولید شده توسط پراش پرتو ایکس (XRD)، اسپکتروسکوپی رامان (RS)، میکروسکوپ الکترونی روبشی (SEM) و میکروسکوپ الکترونی عبوری (TEM) مورد بررسی قرار گرفت. نتایج به دست آمده نشان داد با این روش الماس تک کریستال و پوشش پلی کریستال با کیفیت خوب را می‌توان تولید کرد. مع هذا مجموعه ای از عیوب مختلف مانند دوقلوها، نابجایی ها و نقصهای چیدن همواره در محصولات ایجاد شده وجود دارند.

1. INTRODUCTION

Having spectacular and unique combination of physical, mechanical and chemical properties, diamond/diamond-like carbon (DLC) has become one of the most significant and important materials in the modern technologies of thin films and coatings [1]. Several types of low-pressure chemical vapour deposition (CVD) have so far been proposed and developed for production of diamond/DLC films and coatings [1]. Among these techniques, the oxy-acetylene combustion flame method, which was originally proposed by Hirose and Kondo, possesses several unique advantages. These include a cheap

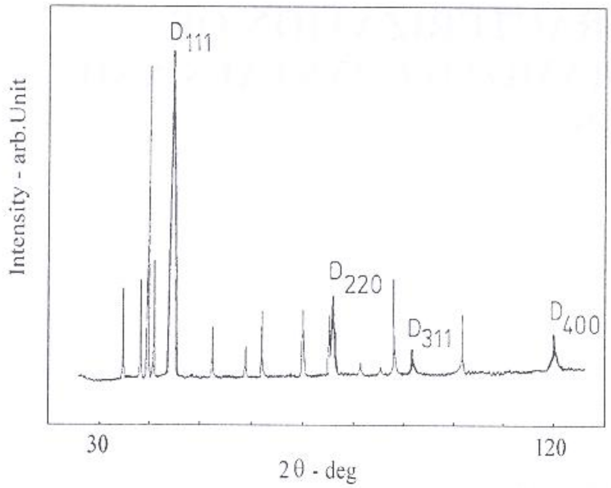


Figure 1. X-ray diffraction pattern obtained from deposited products.

and simple set-up, production of high quality single and polycrystalline diamond, and a much higher rate of deposition (>100um/h), [1-4].

Regarding the quality of diamond/DLC films and coatings, various production parameters are effective. These include; substrate surface preparation and roughness, substrate temperature, thermal gradient on the substrate, nature and ratio of gas mixture, gas flow rate, cooling rate of substrate and film/coating from deposition temperature to room temperature, and chemical specious concentration gradient on the substrate surface [1-8].

It has been shown that the above-mentioned parameters can have effective role on the microstructure and morphological characteristics of deposited diamond/DLC films and coatings [5-10]. In addition, the nature and growth characteristics such as residual stresses, internal defects, predominant crystal growth direction, as well as orientation and texture of grown diamond/DLC are affected by the above-mentioned parameters [6-12].

In this paper, the nature and morphological characteristics of diamond/DLC crystals and films, produced by combustion flame method, have been investigated. In this respect, various techniques including X-ray diffraction (XRD), Raman Spectroscopy, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) were employed and results obtained are presented.

2. EXPERIMENTAL PROCEDURE

The Set-up employed was similar to what has already been used by one of the authors [2-4]. Pure oxygen gas (99.99% O_2) and commercial acetylene gas (C_2H_2) were used. The oxygen to acetylene gas ratio (R) was 0.9 and the total gas flow rate was 2100 ml/min. Deposition time and temperature were 10 min and 1050 °C respectively.

The substrate used was made of pure polycrystalline molybdenum rod and had dimensions of 5mm (h) X 5mm (d). The surface preparation consisted of mechanical abrading using 1200-grit size silicon carbide (SiC) coated paper. All the above-mentioned parameters, such as gas ratio, gas flow rate, deposition time and temperature, as well as substrate surface preparation have determining effects on the quality and the nature of deposited products. Selection of these parameters in the present research work was based on the previous work done by one of the authors and his co-workers [2-4].

The quality and morphological characteristics of the deposited products were examined using a range of techniques, including X-ray diffraction (Philips X-pert, MPD), Raman Spectroscopy, Scanning Electron Microscopy (Jeol 6400) and Transmission Electron Microscopy (Philips 2000 FXII; operating at 200kV).

3. RESULTS AND DISCUSSION

X-ray Diffraction and Raman Spectroscopy

X-ray diffraction pattern obtained from diamond/ diamond-like crystals and films deposited is shown in Figure 1. For this purpose, an X-ray diffractometer with a Ni filtered Cu Kα radiation was used. In addition to the peaks of molybdenum and molybdenum carbides (produced by molybdenum substrate) the XRD pattern shows diamond/-like structure very clearly (Figure 1). In the pattern, very well defined diamond/diamond-like peaks i.e. (111), (220), (311) and (400) are marked. Also, it is observed that the preferred orientation is along the (111) direction.

In the case of results obtained from Raman Spectroscopy, a very sharp and clear peak at 1332 cm^{-1} was obtained (Figure 2). A comparison between the Raman Spectra obtained from grown

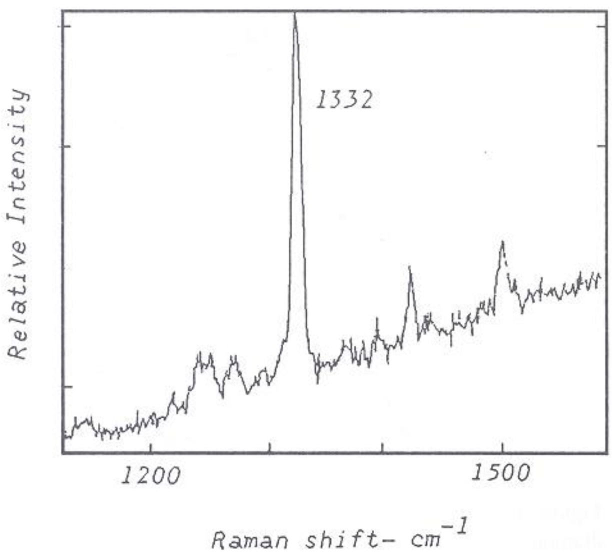


Figure 2. Raman Spectrum obtained from deposited products.

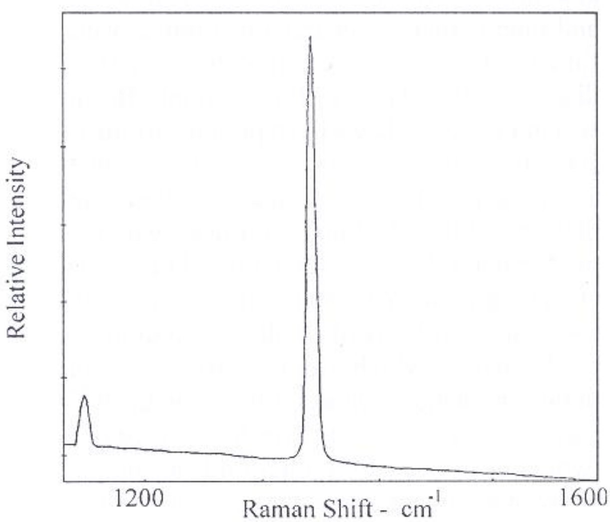
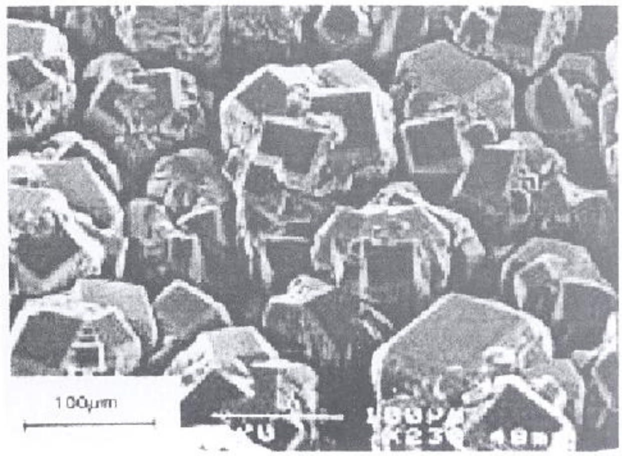
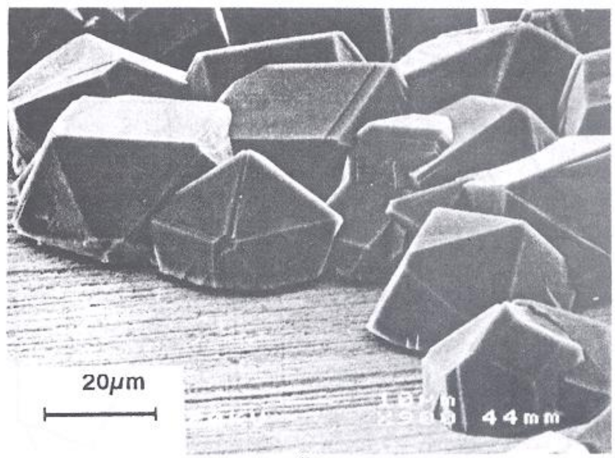


Figure 3. Raman spectrum obtained from natural diamond.



(a)



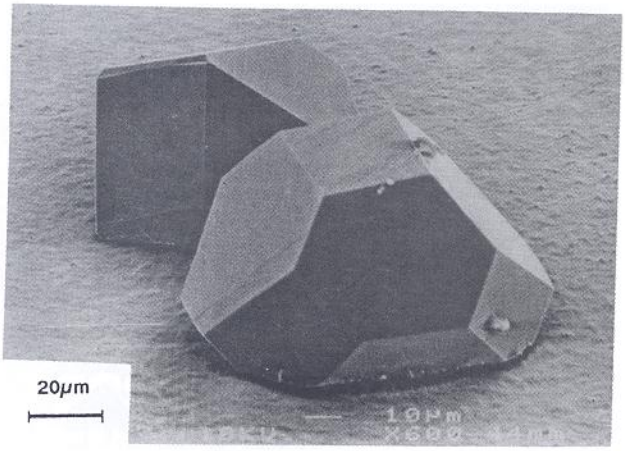
(b)

Figure 4. (a,b) SEM micrograph showing the crystalline nature of deposited diamond.

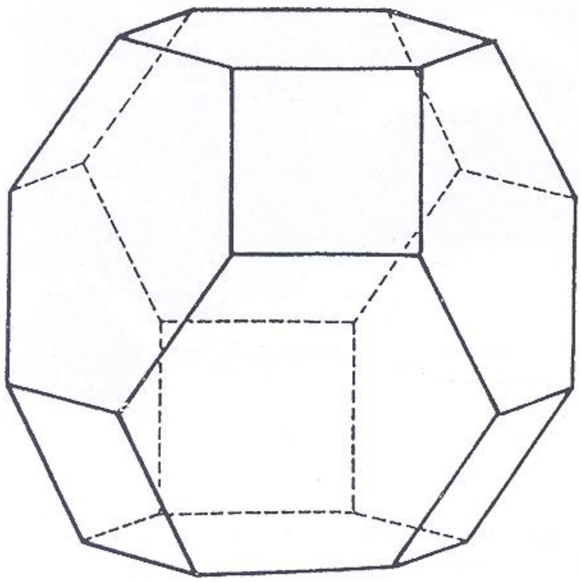
diamond/diamond-like (Figure 2) and natural diamond (Figure 3), reveals the high quality of deposited products. A much smaller peak centered at about 1556 cm^{-1} was also observed on the Raman Spectrum obtained from deposited product (Figure 2). This peak could be attributed to the presence of small amount of amorphous diamond-like carbon.

SEM and TEM Observations The morphology of grown diamond crystals diamond/diamond-like films and coatings would be a function of the oxygen-to-acetylene gas ratio [4]. SEM observation of the crystals and films deposited under the conditions specified in this paper revealed both (100) and (111) orientation of the crystal growth (Figures 4(a,b)). It was also observed that the (111) morphology predominant on the grown crystals and films. This is accordance with the results obtained from XRD patterns (Figure 1).

It was also observed that in some areas polyhedron crystals are formed (Figures 5 (a,b)). This type of crystal is known as the tetrakaidcahehron. This fourteen-faced volume has six-edge faces along with eight hexagonal faces and meets the surface tension requirements of no



(a)



(b)

Figure 5. SEM micrographs (a) and schematic representation (b) showing single polyhedron crystal of diamond.

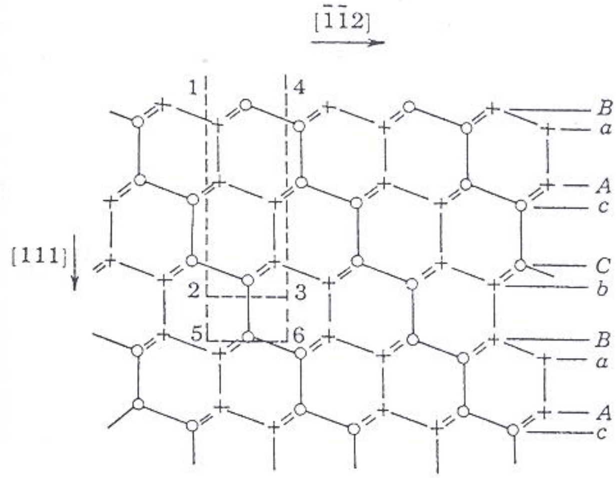


Figure 6. Schematic representation of layer structure of diamond.

more than three grains at an edge and at a corner. A slight double curvature of the eight hexagonal faces satisfies the 120° dihedral angle requirement for three adjacent grains meeting at edge [13]. Stacking faults, however, have been observed in {111} sectors.

The layer structure of diamond contains {111} planes in the sequence Aa Bb Cc Aa Bb Cc, as shown in Figure 6 [14]. It must be noted that the stacking faults in the diamond lattice are the same as in the fcc lattice, i.e., the intrinsic fault is ABC/BCAB, etc.

Transmission Electron Microscopy (TEM) was also utilized for the examination of morphological and microstructural characterization as well as the formation and presence of defects in the grown diamond films. The TEM micrograph (Bright Field, BF) in Figure 7a shows the typical microstructure, i.e. stacking faults in a single diamond grain viewed along the [011] direction in a plain view sample of diamond film. Twining contrast was the most predominant defect observed in all of the diamond crystals grown. A high density of twin, visible as dark line, is observed in this micrograph on two {111} planes, which are in a diffracting condition in this orientation (Figures 7(b,c)). On the diffraction pattern, the two sets of twins have given rise to the twin spots located at one-third of the distance between the major spots from the untwined material. Streaks normal to the {111} plane on diffraction pattern have been also observed. Such streaking can be attributed to the presence of stacking faults or coherent twin boundaries [15]. Dislocations are observed (Figure 8) at Point a and small triangular defects believed to be stacking fault tetrahedral, which are present at Point b. It is believed that the above-mentioned defects could be associated with the residual compressive stresses within the crystals, films and coatings produced during deposition process and/or subsequent cooling to room temperature. Presence of residual compressive stresses within the grown diamond/DLC films and other research workers [6,12] has also reported coatings. It is also believed that the presence of foreign atoms could

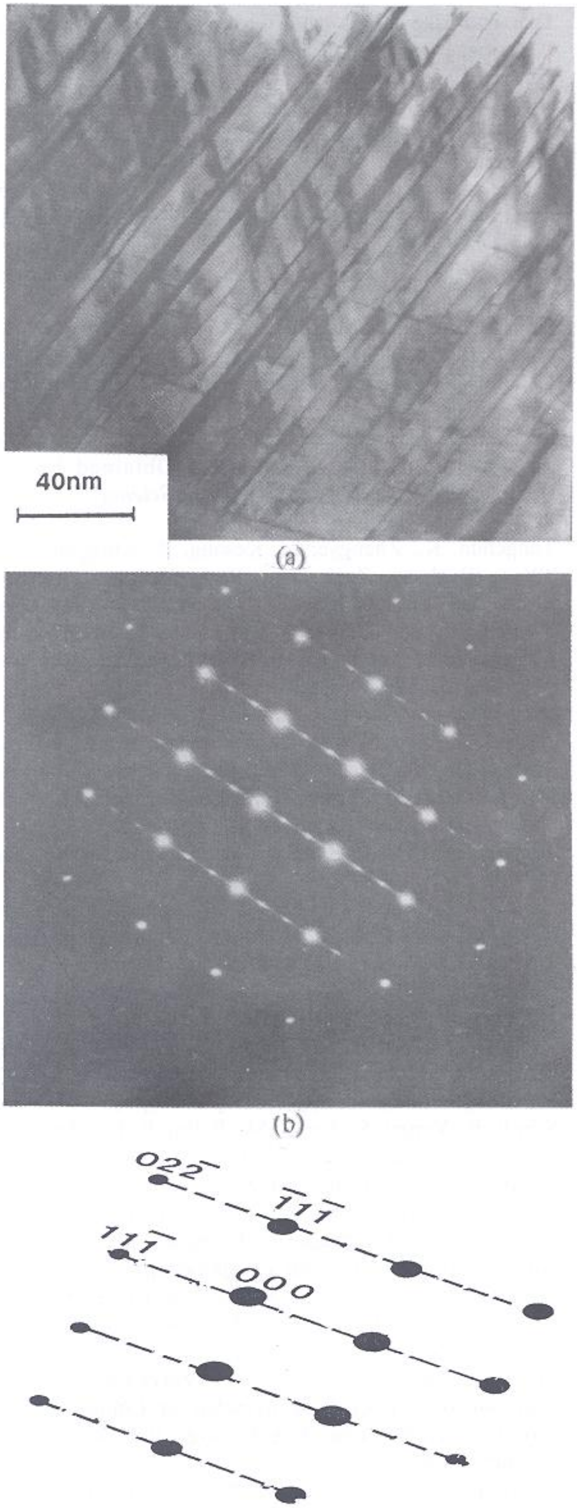


Figure 7. (a) Bright field TEM micrographs showing stacking fault in a single diamond crystal, (b) associated diffraction pattern and (c) schematic representation.

play an important role in this respect. The latter

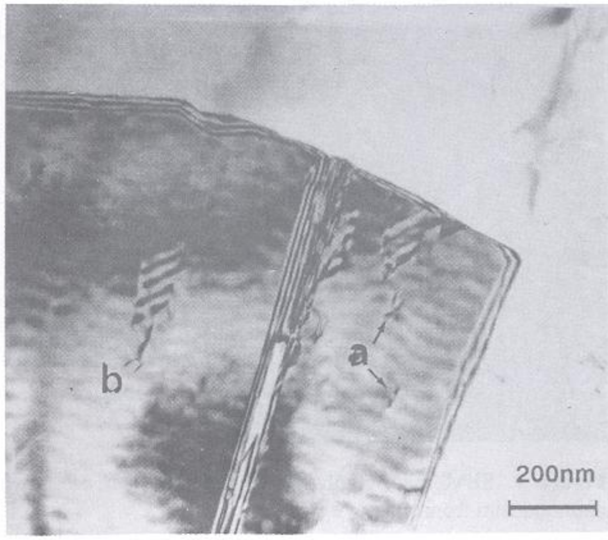


Figure 8. TEM micrograph showing dislocations in grown diamond films. Also small triangular defects believed to be stacking fault are present.

belief stems from two facts: firstly, deposition process within this research work was carried out in air, secondly, the acetylene gas used was a commercial grade one. It has also been reported by other research workers that chemical species concentration gradient on substrate surface have a great influence on the morphology and quality of diamond films [6].

Regarding the residual stresses, the following effects and stress origins are to be considered.

- Thermal stresses due to relatively rapid cooling rate from diamond deposition temperature, i.e. 1050°C, to room temperature.
- Different thermal expansion and contraction coefficients of molybdenum substrate and diamond film.
- Heterogeneous nucleation, as well as the heterogeneous growth rate of various crystals.
- Fluctuating as well as impingement effects of high-speed oxy-acetylene flame on growing diamond film.

Regarding the effect of cooling rate on the residual stresses, it was observed that reducing the cooling rate from deposition temperature to room temperature would increase the bond adhesion strength between the molybdenum substrate and diamond film. Conversely increasing the cooling rate showed a reverse effect. In the case of diamond-coated specimens cooled in cold circulated air to room temperature, cracking, detachment and separation of diamond surface

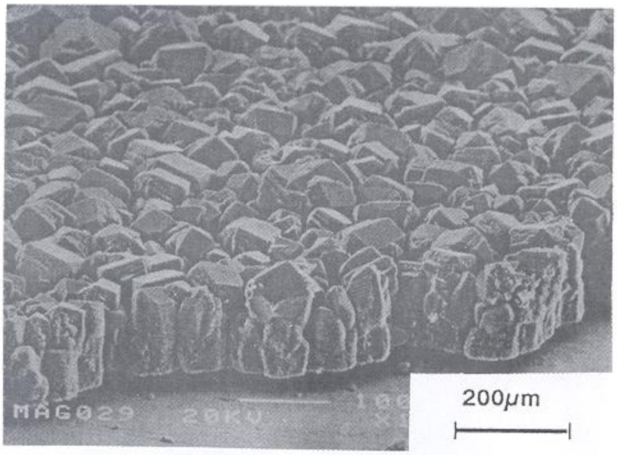


Figure 9. SEM micrograph showing detachment of grown diamond film from substrate surface.

layer was observed. An example of this type of effect is shown in the SEM micrograph of Figure 9. This effect is believed to be due to the high thermal stresses produce during the rapid cooling rate as well as different thermal contraction coefficient of molybdenum substrate and diamond film.

4. CONCLUSIONS

From the results obtained, the following conclusions can be drawn

a) Using combustion flame technique very well defined crystalline diamond films and coatings could be deposited.
b) Deposited diamond crystals showed both (111) and (100) orientations of crystal growth. However, the SEM observations show that the (111) morphology is more predominant.
c) Various lattice defects such as twins, stacking faults and dislocations were observed in grown diamond crystals and films.
d) Presence of lattice defects could be due to a number of parameters such as residual stresses as well as impurity atoms. However, the effect of residual stresses is believed to be much more probable.

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