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Influence of Diamond Purity to Amorphous Growth In-Liquid Plasma Chemical Vapor Deposition (CVD) Method

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ABSTRACT

Diamond is one of the most remarkable natural materials, with several possible excellent physical properties in a wide range of applications. Natural diamonds form under high temperatures and high pressure, at least 250-300 km underneath the earth's mantle. However, diamonds are so rare in nature, so that command a high price. Because of that many researchers tried to grow synthetic diamonds in laboratories to utilize tremendous properties. This research investigates influence of purity of surface single crystal diamond to diamond and amorphous growth using the in-liquid plasma CVD technique. The experiment utilizes a X5CrNi18-10(JIS:SUS 304) substrate pre-embedded with single-crystal diamond seeds. Following deposition, substrate characterization using Scanning Electron Microscopy to observe morphology and Raman spectroscopy to confirm quality of film growth. The impurity at diamond seed can disturbed lattice arrangement such as interstitial, vacancy or substitutional atoms. This reason show that impurities can proposed amorphous growth in deposit film.

Keywords: Amorphous, CVD, Diamond and Growth.

1. Introduction

Diamond is one of the most remarkable natural materials, with several possible excellent physical properties in a wide range of applications. [1]. Such as, hardness, corrosion resistance and wear resistance [2]. Natural diamonds have unique characteristics, they are rarely all present in the same stone [1]. The unique characteristics of diamond made excellent attractive for numerous potential applications [3]. Application of diamonds across numerous fields, including mechanical, electrical, thermal, optical [4], medical device and sensor applications [5].

Natural diamonds form under high temperatures and high pressure, at least 250-300 km underneath the earth's mantle [6]. This intense environment forces carbon atoms to rearrange, becoming more stable as diamonds than their graphite. So, over millions of years, carbon deposits slowly crystallize into single crystal diamonds. This makes diamonds expensive [4]. Therefore, researchers have developed methods to grow synthetic diamonds in laboratories. This process, while complicated, but unlocks the potential of these extraordinary materials for various applications [7]. Chemical Vapor Deposition (CVD) is one of methods to grow diamond synthetic.

CVD methods used to growth of synthesis diamond film has been investigate since 1980s [8]. The interest in CVD diamond films is undoubtedly due to the possibility of synthesizing a wide variety of them [9]. There are two methods for CVD synthesis: conventional or gas phase and in liquid plasma CVD.

Currently research for improving growth rate diamond is still intensively developed. H. Toyota et al. (2008) researched in-liquid plasma CVD for diamond synthesis. In the result, the growth rate with in-liquid plasma is higher than that of conventional gas phase. Because the density of liquid is much higher than that of gas, so the chemical reaction rate in-liquid CVD is much higher than that of gas phase CVD [10]. Therefore, a very high diamond deposition rate (100 μm/h) becomes possible even under low pressure [8] Furthermore, with in-liquid process, the methanol-ethanol solution provides a strong cooling effect that protects the substrate from heat damaged[11]. Gautama, et al. (2016) focused on analyzing the crystal orientation of diamond films. Their research investigated the homoepitaxial growth of diamond films on both orientation (100) and (111) orientations using the in-liquid plasma CVD method. The result of diamond with orientation (100) is higher deposition rate than (111). Furthermore, the dangling bonds effect to diamond growth also has been observed. The diamond surface (100) has two dangling bonds and (111) has one. The surface energy obtained by multiplying atomic density to the number of dangling bonds. If the energy is lower it's easier to form a new interface, so that the polycrystalline growth and become rough surface [12].

However, in previous research never analyze and investigate the influence of surface purity of seed diamond crystal to grow synthetic diamond in in-liquid CVD method. So that, this study tried to investigate influence the purity of surface single crystal diamond to diamond and amorphous growth.

2. Material and Methods

Stainless steel sheet X5CrNi18-10(JIS:SUS 304) was used as substrate in this research. The substrate was precisely cut to dimensions of 8 x 27.5 x 0.5 mm. The substrate was cleaned with ultrasonic cleaning on 20 minutes using acetone, prior to the in-liquid plasma CVD. Single crystal diamond seed was embedded in the cleaned substrate as shown in Figure 1 The

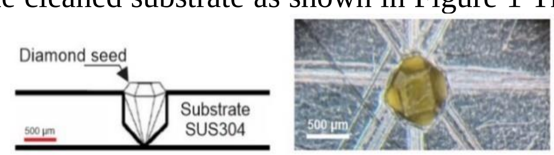
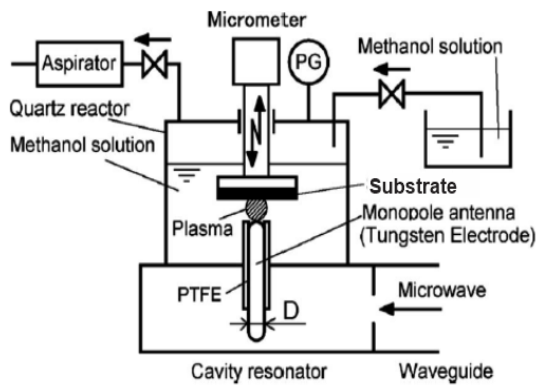


Figure 1. Arrangement of diamond seed and the substrate.

diamond seed in this process made by High Pressure High Temperature (HPHT) process. The last step for preparation by ultrasonic cleaning to ensure pristine diamond seed surfaces. Prior the deposition process the substrate characterized by Scanning Electron Microscopy (SEM : JEOL JSM-6060), Energy Dispersive X-Ray (SEM-EDX), Renishaw in via Raman microscope to characterize of carbon film on diamond seed.

The schematic of experimental set up for in-liquid plasma CVD is shown in Figure 2. The core components include a microwave oscillator operating at 2.4 GHz, a rectangular waveguide, and a cavity resonator, responsible for generating and transforming the microwave energy for plasma creation. The reactor, constructed from quartz glass with an inner diameter of 54 mm and height of 100 mm, houses of plasma, methanol ethanol solution and substrate.



Source: (Toyota, 2011)

Figure 2. Schematic of experimental set up for in-liquid plasma CVD.

The CVD process was conducted under the following conditions: temperature around 800°C, and monitored using an infrared thermometer. The reactor pressure was maintained at 60 kPa and checked using a pressure gauge and controlled by adjusting the valve attached in front of aspirator. The substrate is made of 97:3 solution of methanol and ethanol [8]. The distance between the substrate and electrode was set at 1.5 mm, and the power input was 150 W. The duration for the CVD process was 20 min.

After the CVD process, deposited film on the seed diamonds were characterized by SEM - EDX and Raman spectroscopy (Renishaw in via Raman microscope). SEM provides detailed images of the film morphology and surface features. The SEM observation was performed with voltage of 5-30 kV and magnification of 5-300,000 times. Raman spectroscopy allows in-depth analysis of the chemical composition and crystalline structure of deposit film.

3. Results and Discussions

A SEM image of single crystal diamond seed before CVD process is shown in figure 3. Although both surface of (100) and (111) looks clean, some impurities was detected by EDS analysis on (100), and it was not detected on (111).

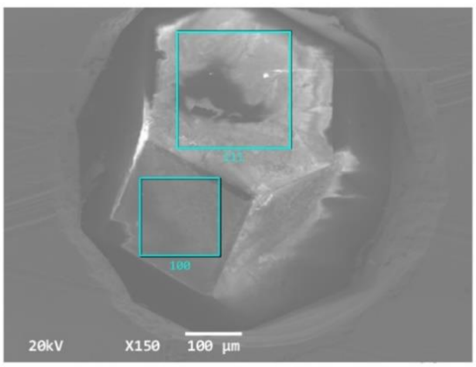
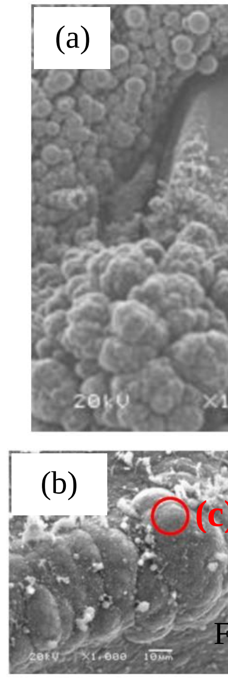
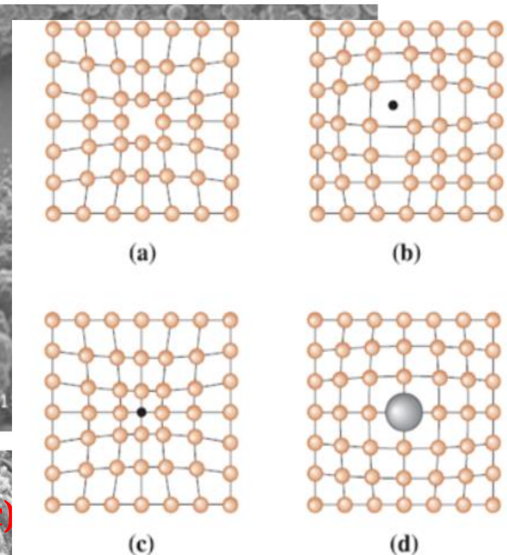


Figure 3. SEM image of single crystal diamond seed before CVD process

A SEM image and a Raman spectrum of the diamond seed and deposit on it after the CVD process is shown in Figure 4. Figure 4 describes that purity of surface influence to growth of deposition film. As shown in Figure 4(a)(b), on the pure side at single crystal (111) deposited film is much somooth. In contrast, The deposites on (100) is larger than that on (111), and cauliflower shape. The Raman spectrum shown in Figure 4(c) indicates the dominant deposit on (100) is amorphous carbon, because overrapped D-band (derived from sp2 bond) and G-band (derived from sp3 bond) are observed. Amorphous structure contains a hybridization of sp2, sp3 [13]. So that, at surface (100) the morphology disordered than (111) which contain structure sp3. The reason for amorpous carbon deposited on (100) is considered the lattice arrangement of carbon in diamond is disturbed due to the presence of impurities through the formation of lattice defects.





Source: (Dhaher, 2019)

Figure 5. The illustration of lattice defect (a) vacancy, (b) interstitial atom, (c)(d) substitutional atom.

Figure 4. SEM image and a Raman spectrum of the diamond seed and deposit on it after the CVD process.
(a):SEM image (×150),
(b):SEM image (×1,000),
(c):Raman spectrum

The illustration of lattice defact shown in Figure 5. These impurities can enter the diamond lattice as vacancies, interstitial atoms or substitutional atoms, which can affect the crystal structure and properties of the material [14]. All of these defects discard the arrangement of the surrounding atoms and create a strain in the crystal structure. First, vacancies or removal of carbon atoms from the diamond lattice. Second, impurities atom may enter the diamond lattice as interstitial atoms, occupying sites that are not normally occupied by carbon atoms. Third is substitutional atoms can also replace carbon atoms in the diamond lattice, leading to the formation of substitutional impurities. So that, impurities can stimulate amorphous growth at diamond deposition process in liquid plasma CVD method.

4. Conclusion

The impurity of surface can trigger amorphous growth cause impurity made disturbed lattice arrangement such as interstitial, vacancy or substitutional atoms. So that, The pristine at diamond seed is one of parameter that influence to diamond deposition in liquid plasma CVD method.

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