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Growth strategies for large and high quality single crystal diamond substrates

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ABSTRACT

The high pressure (130–240 Torr) and high power density microwave plasma assisted chemical vapor deposition (MPACVD) of single crystal diamond (SCD) substrates is investigated. Locally controlled growth strategies that enable the synthesis of large (~5 mm) and thick (200 μm–1.3 mm) CVD free standing SCD substrates are presented. Two process control methods, i.e. control of the input power level versus time, and the precise control of the substrate holder geometry when combined play an important role in obtaining high quality free standing single crystal diamond (SCD) substrates. The performance of one distinct substrate holder design, the "pocket holder", is presented in detail and is compared to the performance of the more commonly used open holder. A comparison of these two holder designs operating in the high pressure SCD synthesis process environment reveals the advantages of the pocket holder. The pocket holder design not only aids in the growth of thick SCD substrates when operating within the reactor's safe and efficient operating regime, but also enhances their *in situ* lateral growth. Processes are described which enhance the growth of the SCD surface area while simultaneously reducing the growth of the polycrystalline diamond rim that typically surrounds the synthesized SCD. Using such methods at 240 Torr MPACVD SCD plates and SCD cubes are synthesized at high growth rates.

1. Introduction

Currently microwave plasma assisted chemical vapor deposition (MPACVD) is the most prominent method for synthesizing single crystal diamond (SCD) substrates [1–4]. Different diamond deposition methods utilizing the MPACVD technique have been employed for the purpose of investigating the synthesis of high quality, large area single crystal diamond plates. For example, Tallaire et al., [5] have proposed controlling growth by controlling the evolution of the different crystal faces to produce a large defect free, top crystal surface. Mokuno et al., [6,7] have proposed to use alternative diamond growth steps on the top and the sides of the initial seed, first to enlarge the initial diamond seed surface and then ultimately to produce a large diamond substrate. They also observed that during growth on a single seed in an "enclosed holder", the SCD growth surface initially slightly increases during the first 1/2 to 1 mm of growth and becomes surrounded by a polycrystalline diamond (PCD) rim and the top SCD surface itself becomes enclosed by a thick PCD rim. Then as the diamond growth continues the SCD growth surface continually deceases as the PCD rim thickness increases and encroaches into the SCD top surface. Thus the formation of the PCD rim limits the size and cross sectional area of the synthesized SCD. Yamada et al. [8–10] numerically investigated the influence of varying the substrate geometry and discharge position on the local synthesis environment and the final SCD synthesis results. They found that if the microwave discharge is located close to substrate it is modified by the presence of the substrate and the substrate holder design. As a result, one can infer that the diamond synthesis process itself can be modified by varying the local substrate design/geometry. They also point out that the substrate temperature distribution on the top surface of the substrate most importantly controls the local diamond synthesis process. Recently Yamada et al. [11–13] have combined the growth of "mosaic crystals", which was first proposed by M.W. Geis et al. [14], with an ion implantation lift-off method to obtain over one inch single crystal diamond plates.

While much progress has been made in the synthesis of SCD substrates each of these methods has problems such as limited growth size, growth process interruptions, stress and cracking, etc. When growing thick crystals, a limiting condition for all of these methods is the formation of non-epitaxial features on the corners, on the edges and on the top of the growing crystal surfaces. Ultimately this leads to the formation and growth of a PCD rim which surrounds the top growing surface. Additionally in order to be cost effective any process that is developed must deposit high quality SCD at a fast growth rate so that the growth can be carried out in a reasonable time and at a reasonable cost. This growth rate condition requires that MPACVD synthesis be carried out at high pressures (>150 Torr) and with the use of a high power density microwave plasma [15–17]. Thus, much development still remains in

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order to achieve the routine synthesis of large, thick and high quality SCD substrates suitable for industrial applications.

Recently we have reported that when using high pressure and high power density microwave discharges, if efficient and repeatable MPACVD diamond synthesis is desired then it is important to design and operate the microwave reactor system in such a way that high microwave coupling efficiencies are achieved [18] and then operate the reactor within a "safe and efficient" process regime [15–17]. Our MPACVD experiments have also demonstrated that it is necessary to spatially control the "local" process environment around and in the vicinity of the substrate. One of the ways this can be achieved is by modifying the local discharge geometry conditions such as developing optimized substrate holder designs. In addition, as the process proceeds versus time it is also necessary to spatially control the "local" process conditions versus time adjacent to the plasma–substrate boundary layer in order to maintain the proper substrate deposition temperature and to avoid the formation of discharge hot spots [19].

2. The experimental microwave reactor and microwave system

The experiments presented here were performed with two different 2.45 GHz microwave cavity plasma reactors (MCPR). These reactor systems are identified here as reactor B and reactor C, and have been described in more detail elsewhere [16,17]. In order to ensure high diamond growth rates and high discharge power density deposition conditions, all experiments were carried out in the high pressure deposition environment. Experiments were performed preferably at 240 Torr and the substrate holder was water cooled by a variable position cooling stage. However some experiments using the open holder had to be performed at reduced pressures of 130–160 Torr in order to prevent the formation of discharge hot spots and process runaway. The experimental results described here were obtained while the reactors were operated within the safe and efficient operating regime [17,18].

3. Experimental procedures

The experiments discussed here have been performed on <100> oriented 3.5 mm × 3.5 mm × ~1.4 mm HPHT type Ib seed substrates. All the seeds used in the experiments discussed in this paper have a top surface area of 3.7 × 3.7 mm^2. They are first cleaned with a mixture of nitric and sulfuric acids, then with hydrochloric acid and are finally ultrasonicated in acetone and then in methanol before loading them into the reactor. Once the substrate is loaded into the reactor, the system is pumped down for 12 h to reach the base pressure of ~1 mTorr. During the deposition process a gas feed mixture of hydrogen and methane gases with a purity of 99.9995% and 99.999% respectively is used. Any nitrogen that is present during the synthesis experiments is due to the impurities in the feed gases and any slight leaks in the vacuum system. Nitrogen gas was determined to be limited to <6 ppm in reactor B and ~10 ppm in reactor C.

During the growth process the surface temperature (T_s) is measured with a 0.96 μm wavelength monochromatic optical pyrometer (IRCON Ultimax Infrared thermometer) with an emissivity of 0.1 and a minimum spot size of 2 mm. The setup of the pyrometer is discussed in references [17,18].

4. Controlling the reactor versus time to achieve a constant substrate deposition temperature

During all the SCD synthesis experiments described here SCD grows on the single crystal substrate surface and a layer of PCD is deposited on the surface of the molybdenum substrate holder. The additional deposited SCD and PCD alters the plasma substrate boundary layer and the reactor behavior varies or drifts slightly versus deposition time, i.e. the reactor operating field map curves [15,17,20] vary versus time as is shown in Fig. 1. Then the initial process temperature increases from the A to B operating points. Thus the substrate temperature increases

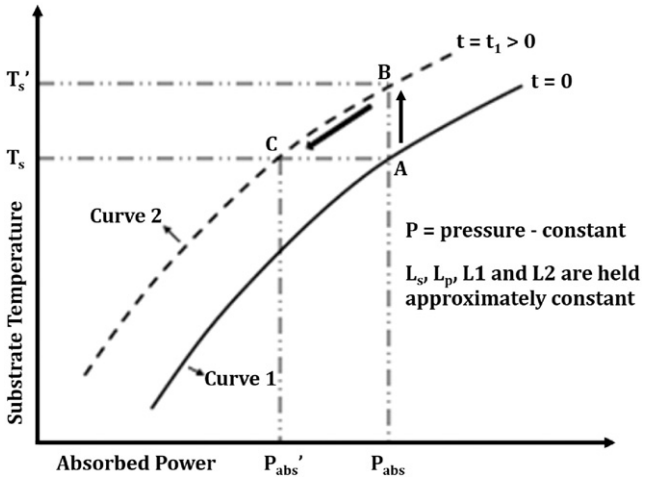

Fig. 1. Controlling the input power versus time to achieve constant substrate temperature versus time. The temperature is held constant at the initial temperature by moving the reactor operating point from A to C as the absorbed power is slowly and continuously reduced during the process cycle.

versus time as the PCD layer grows and as the SCD substrate thickness increases. In Fig. 1, L_s and L_p refer to the short and the probe length of the cavity and L1 and L2 lengths determine the substrate position [17]. PCD is deposited on the molybdenum substrate holder and the seed surface temperature increases from T_s to T_s', where $T_s' - T_s < 100$ °C. The operating field map curves vary slightly as time increases from t_0 to t_1 and the reactor operating point varies from A to B (see curves 1 and 2 in Fig. 1). However for the typical SCD process it is desirable to hold the substrate temperature approximately constant over the entire synthesis cycle. This can be achieved by adjusting the reactor operating conditions and the reactor geometry versus time to compensate for these substrate and substrate holder physical changes and associated temperature changes.

As is shown in Fig. 1, the operating field map curves vary from curve 1 to curve 2 as the process evolves with respect to time. The substrate temperature can be held approximately constant by slightly adjusting the absorbed power versus time. For example by reducing the absorbed power by just 50–100 W the substrate temperature can be held constant. The absorbed power can be adjusted by using any of the three different ways. The most common way is to just directly vary the incident power by adjusting the microwave generator output. This is indicated in Fig. 1. The second and third methods of input power variation (not shown in Fig. 1) are by holding the incident power constant and by varying the operating pressure and/or slightly varying L_s to detune the reactor from a match. The variation of L_s mismatches the reactor and slightly increases the reflected power (P_{ref}). See reference [18] for the details on reactor tuning. In all the experiments reported here, the method used to hold the substrate temperature constant versus time was by varying the microwave generator power.

5. Single crystal diamond synthesis

5.1. Open holder SCD synthesis

A series of diamond synthesis experiments were performed in reactor B using the open substrate holder design. In the open holder synthesis process geometry, the HPHT seed is placed directly on a flat, water-cooled molybdenum substrate holder as shown in Fig. 2(a). During synthesis the top, edges and the side surfaces of the seed are directly exposed to the active discharge and to the impressed microwave electric fields that exist in the substrate–discharge boundary interface. It is well known that at lower pressure operation (<150 Torr) the open holder geometry synthesizes SCD crystals that are surrounded by a