Diamond & Related Materials 66 (2016) 36–46

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Analyses of single crystal diamond substrates grown in a pocket substrate holder via MPACVD

Shreya Nad [a,b], Jes Asmussen [a,*]

[a] Department of Electrical and Computer Engineering, Michigan State University, East Lansing, MI 48824, United States
[b] Department of Physics and Astronomy, Michigan State University, East Lansing, MI 48824, United States

ARTICLE INFO

Article history:
Received 27 August 2015
Received in revised form 2 March 2016
Accepted 13 March 2016
Available online 16 March 2016

Keywords:
Single crystal diamond
MPACVD
SCD characterization
Etch pit density
SCD synthesis

ABSTRACT

High quality single crystal diamond (SCD) substrates are required for several different important current applications. Microwave Plasma Assisted Chemical Vapor Deposition (MPACVD) is a convenient deposition method for high quality substrates. It is hence imperative to synthesize and analyze substrates grown via different CVD techniques. This paper describes the quality of single crystal diamond substrates which have been grown via one such deposition strategy, which is in a "pocket substrate holder" design. The growth process in such a holder helps in depositing substrates which have almost no polycrystalline diamond (PCD) rim growth. The exact pocket holder growth process at high pressures (240 Torr) and high microwave power densities (~ 500 W/cm^3) has been discussed in a previous publication [1]. The SCD CVD substrates were analyzed with different characterization techniques. By synthesizing diamond substrates in a pocket holder, the lack of any/almost any PCD rim helped in reducing the amount of stress in the crystals. To study the electronic quality of the substrates, etching experiments were conducted to determine the etch pit density. Nomarski images confirm that the number of etch pits at the edges is higher than at the center of the etched surface thereby implying the feasibility of this simpler method of reducing the etch pit density. The pocket holder process thus not only reduces the PCD rim but also reduces the substrate etch pit density and hence shows good promise of delivering high quality substrates.

1. Introduction

Novel materials with better mechanical, optical, and electronic properties are the need of the hour for many applications in the real world. Diamond is one such material and has many exciting properties such as high thermal conductivity, chemical inertness, extreme hardness and electrical insulation. These properties have been exploited for several years in many different applications like optical elements [2], high energy beam detectors [3] and heat spreaders [4] among many others. Currently most applications suffer from the availability of high quality (<100 ppb nitrogen impurity), thick (>400 μm), large (>1 cm^2), low birefringence and low stressed single crystal diamond (SCD) substrates. In order to produce large SCD substrates the most convenient deposition method thus far is the MPACVD diamond synthesis process [5] which provides a suitable thermal and chemical environment for the growth of high quality SCD substrates at high growth rates.

Recently several diamond research groups have attempted to grow large area, high quality SCD plates/substrates. Researchers from AIST, Japan have developed a substrate lift-off process, side surface (100) growth processes, and a mosaic wafer growth process. These processes have shown good promise of enlarging the SCD surface area ([6–12]). Diamond growth studies performed by LSPM–CNRS, France by utilizing high growth rate, beveled HPHT diamond seeds and multi-step CVD diamond growth have also been successful in synthesizing large SCD substrates ([13–19]). The characterization and analysis of the substrates grown by these research groups indicate that they are of good quality. The absorption coefficient measurements by FTIR and UV/Vis spectroscopy show that the substrates have very low level of nitrogen content such that it is not detectable by these techniques ([13–16,20]). Photoluminescence spectroscopy of these substrates also indicates no luminescence due to nitrogen and silicon defects. But while these growth strategies do deposit substrates with low impurity content, the synthesized crystals suffer from cracking and stress ([16,21]). This is due to the fact that a major lingering problem in these deposition techniques has been the simultaneous growth of a PCD rim around the SCD substrate. This not only leads to stress in the crystals but also reduces the final SCD surface dimensions due to the growth of non-epitaxial defects around the edges ([16,22]).

In an effort to solve the polycrystalline rim issue, a "pocket substrate holder process" that prevents/minimizes the growth of a PCD rim has been investigated in a previous publication [1]. This process includes the following steps: (1) placing the substrate in an optimized "pocket holder" geometry and then (2) applying the correct sequence of microwave plasma processing steps. Synthesis occurs when the substrate is placed in a pocket and its edges and corners are shielded from the

* Corresponding author.

http://dx.doi.org/10.1016/j.diamond.2016.03.007
0925-9635/

applied electromagnetic fields and the associated intense plasma. Rimless or almost rimless diamond is then produced. The question that remains then is what is the quality of the diamond grown by this method. Thus, the major objective of this paper is to analyze the SCD plates and as-grown substrates deposited in a pocket holder. Hence in this paper, the characterization results of high quality SCD substrates synthesized in a pocket holder are presented.

2. The SCD experimental growth process

2.1. SCD experimental system

The deposition processes of all single crystal diamond substrates discussed in this paper have been carried out in a microwave cavity plasma reactor (MCPR) developed at Michigan State University. The design of this MCPR, known as reactor B, and the reactor variables are described extensively in references ([23,25–27]). In order to increase the growth rates, the synthesis process has been carried out at a high deposition pressure of 240 Torr. At these high pressure levels, the microwave discharge becomes extremely intense and the plasma volume decreases at high power levels of 1.8–2.2 kW. For 240 Torr, the microwave discharge power density was calculated to be ~500 W/cm^3 ([23,24]). All deposition processes in reactor B were performed within the safe and efficient operating regime ([23,24]). Additionally, in all experiments, the reactor and the associated processes were operating under optimized conditions, i.e. with microwave power coupling efficiencies of more than 95%. The details about the microwave power coupling process have been discussed elsewhere [28].

2.2. Substrate holders used for synthesis

It has been observed that the substrate holders play an important role in the deposition of large SCD substrates ([1,22,29]). The more commonly used open holders, in which the substrate is placed in direct contact with the microwave discharge, lead to the formation of a PCD rim. This PCD rim not only reduces the useful SCD surface area but also leads to the formation of defects on the SCD surface especially at the edges. In order to increase the CVD SCD surface area and to improve the quality of the synthesized substrates, we use the pocket holder design shown in Fig. 1, where the walls of the recess prevent or minimize the formation of any rim on the seed substrate. All such holders are made of molybdenum and polished on both sides to obtain smooth surfaces. The critical factors 'd' and 'w' in such pocket holders (Fig. 1), as has been discussed in reference [1], play an important role in depositing almost rim free CVD SCD substrates. For such substrates, depending on the deposition time, typically 'd' = ~1.5–2.6 mm and 'w' = ~0.5–1 mm. The growth process in these pocket holders has been discussed in greater detail in ([1,29]).

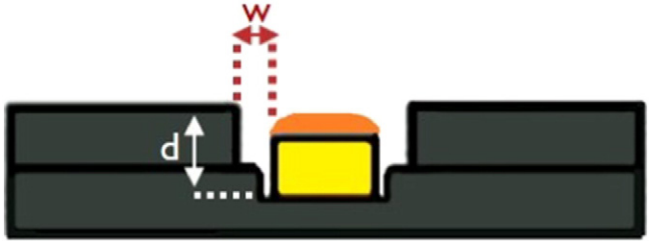

Fig. 1. Pocket holder design for SCD synthesis. The yellow box indicates the cross section of a HPHT seed placed within a recess and away from the intense plasma region. (Reproduced with permission from reference [1]).

2.3. Substrate cleaning process

All SCD growth steps have been carried out on 3.5 × 3.5 × ~1.5 mm^3 <100> oriented HPHT type Ib seeds from Sumitomo. The growth process was preceded by careful chemical and plasma treatment procedures [28] in order to reduce the defects and impurities on the substrate surface prior to growth. The seeds were first subjected to an acid cleaning process with a mixture of sulfuric and nitric acids and then with hydrochloric acid. This cleaning step was then followed by a final rinsing step with ultrasonication in acetone and then in methanol. The seed was then rinsed and air dried for further pre-growth treatment.

2.4. Plasma etching of substrate

Following the acid and solvent pretreatment of the seed, it was loaded into the reactor and then the surface of the seed was plasma etched in a pure hydrogen plasma discharge at 180 Torr for 1 h. The reactor was then pumped down for half an hour. This hydrogen plasma pretreatment of the HPHT seed serves two purposes: (1) it removes impurities on the surface of the seed which are then pumped out of the system, and (2) it reduces/removes any polishing damage on the seed surface. This etching process thereby helps in preparing the seed for growth to proceed on a clean surface with less number of defects.

2.5. SCD growth process

After the plasma pretreatment of the HPHT seed, the pressure was increased with the addition of hydrogen gas and a hydrogen plasma was reignited at ~5 Torr. The power level and the substrate temperature were then gradually increased with the increasing pressure. Once the required process pressure level was reached, the incident power was adjusted to maintain a constant substrate surface temperature. After 10 min of plasma etching in a pure hydrogen discharge at 240 Torr, the methane gas was flowed into the quartz bell jar to begin the growth process. The SCD results discussed here have been synthesized at a fixed pressure level, % CH_4/H_2, total flow rate (f_t) and within a fixed substrate temperature (T_s) range measured by a one color pyrometer with an emissivity of 0.1 and a fixed incident power (P_{inc}) range and with a nitrogen impurity of ~6 ppm in the total gas flow due to gas impurities. A list of the as-grown CVD substrates and plates (given by a suffix "C" at the end of the substrate name) discussed in the following Sections 3.1 to 3.2.4 are given in Table 1.

Process control of the different input and output reactor variables during growth serves a crucial role in the synthesis of high quality CVD SCD substrates. During the entire process cycle the input power was slightly adjusted to maintain a constant surface temperature between 1100 and 1150°C ([1,29]). As the single crystal diamond substrate increases in thickness during growth, the substrate temperature also increases. This is due to the modification in the local growth conditions when the boundary layer between the substrate and the discharge changes slightly with the growth time. Hence, in order to maintain consistent local growth conditions during the entire synthesis process, it is imperative to adjust the incident power level with time [1].

2.6. SCD post growth processing steps

At the end of the growth process, the final substrate was cleaned with a mixture of nitric and sulfuric acids and then rinsed by ultrasonicating it in methanol. After the initial characterization steps of linear encoder measurements for growth rate and weight gain measurements, optical microscopy, and atomic force microscopy, the "as grown" SCD substrates were laser cut to separate the CVD grown single crystal plates (here referred to as CVD SCD plate) from the HPHT seeds. Then the plates were mechanically polished to reduce roughness on both sides of the plates [30]. The CVD SCD plates were then further characterized using UV/Vis and FTIR spectroscopy,