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Single Crystal Diamond Growth by Microwave Plasma Chemical Vapor Deposition System

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Abstract

This study delves into the diamond growth process on distinct substrates, namely Seed A and Seed B, fabricated using different production methods from separate companies. Seed A, employing ion implantation and the lift-off method akin to semiconductor production, stands distinct from Seed B. Preceding the growth phase, thorough chemical cleaning was administered to the substrates to mitigate potential organic or inorganic contamination from laser cutting, polishing, and surface fabrication. The diamond growth was executed utilizing the MWCVD system, where plasma was generated under 5 Torr pressure and a 500W microwave power. The investigation focused on understanding the impact of diamond growth rates under varying CH_4/H_2 gas ratios. Substrates were strategically placed on the molybdenum surface using "mosaic growth" methods, ensuring no gaps between them. Photoluminescence spectra for Seed A and Seed B were meticulously examined to unravel insights into their respective characteristics. Additionally, this study pioneers a novel approach, coating the molybdenum surface with AlTiN and TiN using the physical vapor deposition (PVD) method. This innovative surface modification, a first in the literature to the best of our knowledge, aims to enhance the properties and performance of the diamond growth process. The findings of this comprehensive study contribute to the evolving understanding of diamond growth dynamics on different substrates and introduce a novel surface modification technique, opening avenues for further advancements in diamond film applications.

Keywords: Synthetic diamond, CVD, PVD

INTRODUCTION

Technological progress has played a pivotal role in shaping human history and transforming our lifestyles. The ongoing quest for technological advancements is driven by the aim to address significant challenges and enhance the quality of human life. The future application of diamonds is a topic undergoing continuous research and development. Given that the natural formation of diamonds requires extreme pressure and heat, their resources are inherently limited. The current research landscape is grappling with the dual challenges of depleting natural resources and the escalating costs associated with production and processing.

The increased cost of diamond extraction from mines not only impacts economic considerations but also poses ecological threats to the environment. Consequently, there is a heightened focus on synthetic diamond production to meet the growing demands of technology while circumventing the issues associated with natural diamond production. The covalent bond's high strength (347 $kJ.mol^{-1}$) necessitates a substantial amount of energy to remove a carbon atom from the diamond lattice, contributing to the diamond's renowned hardness and wear resistance (Nassau, 1979).

In the 21st century, significant strides have been made in the technology for producing high-quality synthetic diamonds. Laboratory-grown synthetic diamonds are indistinguishable from natural diamonds in terms of their chemical, optical, and physical crystal structure. While both types consist of bonded carbon atoms, the distinction lies in their formation processes. Synthetic diamonds entered mass production in the early 2000s, primarily utilizing the HPHT (High Pressure High Temperature) or CVD (Chemical Vapor Deposition) methods (Werner, 1998).

Historically, the HPHT method dominated synthetic diamond production. Operating in the natural diamond growth environment, this method involves temperatures ranging from 1000 to 2000°C and pressures in the GPa range. However, HPHT has limitations, including restricted crystal size and impurities, particularly nitrogen, which affects the potential for electronic applications. Conversely, the CVD method operates at lower pressure and temperature compared to HPHT. It results in both diamond and graphite production in a metastable carbon regime, with conditions optimized for quality diamond growth (Koizumi, 2008).

The CVD technique offers advantages over HPHT, allowing greater customization for growth requirements, enhanced purity of diamond crystals, and the incorporation of doped elements for electronics. While HPHT diamonds may contain more metallic inclusions due to the production method, graphite inclusions are primarily observed in CVD diamonds based on the purity of the gas used.

This study specifically explores diamond production via the CVD method, experimenting with different methane/hydrogen flow rates to achieve varying results. Also, in this study homoepitaxial growth of diamond films was investigated using the MWCVD method using 100-oriented diamond substrates mosaic growth method. In addition, the effect of substrate quality different methane/hydrogen flow rate on growth effect will be investigated in the study. For the first time in the literature, in this study, diamond growth by coating with molybdenum substrate holder PVD method was investigated.

MATERIAL AND METHODS

Substrate Preparation Before Growth

The height precision of all substrates intended for growth is a critical factor, with a carefully selected tolerance of ± 0.03 mm when placing them in the reactor ring. The uniformity of plasma distribution between substrates hinges on this precise height alignment. Failure to achieve a homogeneous plasma distribution can impede the establishment of heat balance during the growth process.

Once substrates of suitable height are selected, the possibility of organic or inorganic contamination arises from laser cutting, polishing, and substrate production. To address this, a chemical cleaning process is employed, which is consistent across all diamond growth procedures. The cleaning steps are outlined below:

1.Acidic Cleaning:

Nitric acid (40 mL) and sulfuric acid (40 mL) are mixed in a pyrex beaker, which is then heated to 500°C and left for 30 minutes. The substrate is subsequently rinsed with deionized water. Hydrochloric acid (40 mL) is placed in a pyrex beaker, heated to 500°C, and left for 15 minutes. The substrate is then rinsed with deionized water. Ammonium hydroxide (40 mL) is placed in a pyrex beaker, heated to 500°C, and left for 15 minutes. The substrate is rinsed again with deionized water. Following this process, the substrates are positioned in the polarizer.

2.Ultrasonic Cleaning:

Initially, ultrasonic bath cleaning is conducted with acetone (30 mL) in a pyrex beaker for 15 minutes. Subsequently, ultrasonic bath cleaning is performed with methanol (30 mL) for an additional 15 minutes in a pyrex beaker.

3.Final Rinse and Drying:

Substrates undergo a final rinse with deionized water. Nitrogen gas is employed to blow-dry the substrates, effectively removing any residual water. After completing the cleaning process,

the substrates are positioned on the molybdenum surface of the substrate holder and then onto the reactor ring.

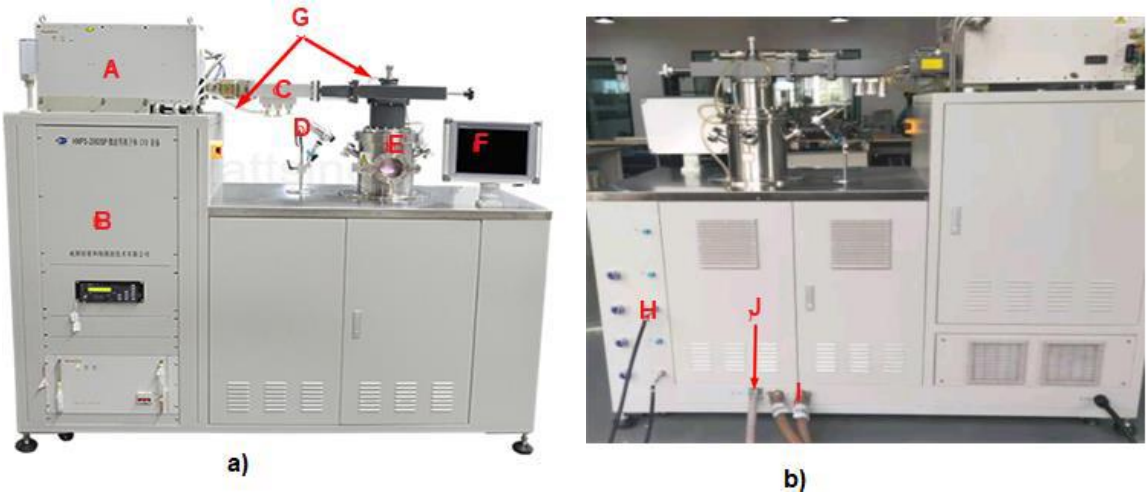

Figure 1. MWCVD system

A) Solid State Microwave Generator (0.5~6kW, MW frequency 2450MHz±50MHz)
B) Electronic Panel and Power System
C) Microwave Waveguide
D) Infrared Pyrometer (300~1400°C)
E) Reactor Circle
F) Magnification Control Screen
G) Cooling Water Inlet Lines
H) Gas Inlet Line
I) Chiller Cooling Water Inlet and Outlet
J) Exhaust Line

In the system given in Figure 1, in the process, “Edwards E2M28 Rotary Vane Vacuum Pump" vacuum pump was used to vacuum the reactor ring. This pump, the reactor ring can be vacuumed up to a pressure value of 5x10-3 Torr. "ER-4.0 Water Cooled Chiller" was used for water cooling of the Microwave Generator and Reactor. It provides the 22 L/min water flow required for the MWCVD system.

After the bottom substrate cleaning/preparation process, 7x7x0.3 mm (100) oriented diamond bottom substrates were placed appropriately in the bottom substrate holder with the method known as "mosaic growth", leaving no space between them (Wang, 2019). The lower substrate holder was carefully placed in the reactor chamber Figure 1. and the vacuum chamber was

closed. The vacuum pump was turned on and for growth was vacuumed until it reached the pressure value of 5x10-3 Torr. The reactant gases to be used in the reactor were opened. The hydrogen generator used as the hydrogen source in the system was started. MW power supply, flow rate of cooling water entering the system and cooling degree of the chiller were checked. The microwave generator was turned on and allowed to warm up for 2-3 minutes. Hydrogen plasma was created by introducing hydrogen gas into the reactor chamber. When the pressure reached 5 Torr, plasma was created by applying 500W power. Reflected power should be kept to a minimum. Depending on the quality of the substrate, if there is any visible dust, pollution, etc. on the substrate, it is cleaned from the surfaces using hydrogen/oxygen gas. When the pressure and MW power were reached to target values, methane gas is gradually added to the hydrogen plasma and accumulation begins on the surface of the lower substrates.

400h (CH_4/H_2 gas flow rate) of growth after the required thickness is reached the coating process begins. Methane gas flow is cut off. Pressure and power are gradually reduced. The closing process should be quite slow. If the lower substrates and the lower substrate holder are cooled too quickly, stress may occur during growth, cracks may occur, or diamond-like structures on the lower substrate holder surface may break off and stick to the surface of the lower substrate and cause inclusions. When the pressure reaches 5 Torr, microwave power is turned off and the flow of hydrogen gas is stopped. After waiting 15-20 minutes, the vacuum is broken and the vacuum chamber is opened and growth samples are taken.

This study, which is a pioneering study in the scientific literature, used the Physical Vapor Deposition (PVD) method to coat AlTiN and TiN on the molybdenum surface. In order to prevent diamond-like structures from accumulating in the empty spaces on the lower substrate holder surface, the molybdenum surface was coated with different thicknesses using the PVD method and diamond films were growth.

RESULTS AND DISCUSSION

In the realm of epitaxial crystal growth, the quality of the substrate employed is a paramount factor influencing crystal quality. Defects arising in the crystal during substrate production can have detrimental effects on the crystal structure during growth, leading to issues such as stress, lattice mismatch, and dislocations in the resultant structure.

In the context of this study, two distinct companies, Seed A and Seed B, provided different substrates manufactured through divergent production methods. Seed A employs ion implantation and the lift-off method, a widely utilized technique in semiconductor production. The schematic representation of the Seed A production method is illustrated in Figure 2. The

uniqueness of Seed A's production method sets it apart from Seed B, with the former leveraging ion implantation and lift-off techniques to create substrates for epitaxial crystal growth.

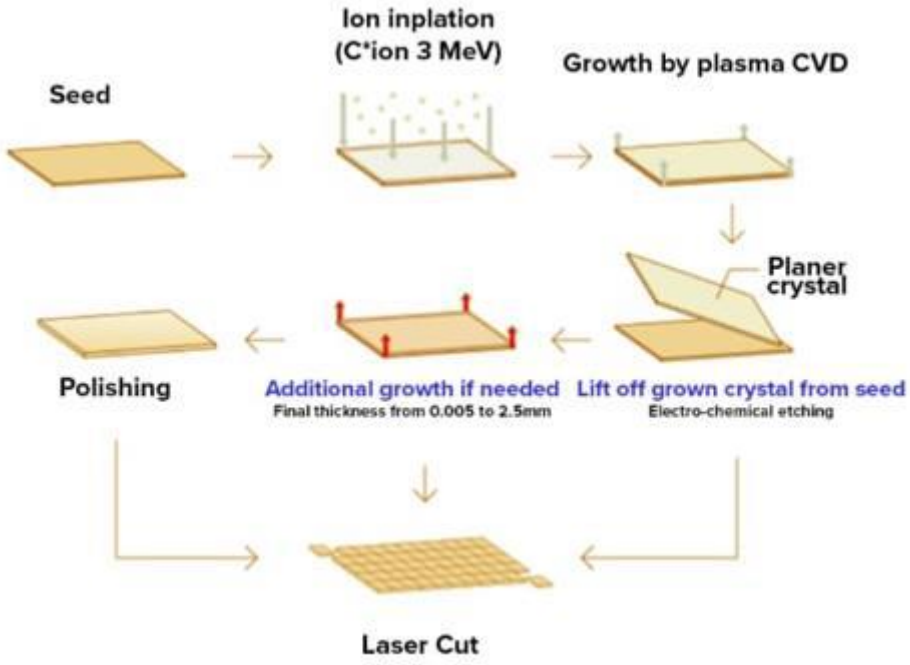

Figure 2. Substrate production with lift-off process

The distinctive photoluminescence peaks associated with diamond were observed in both substrates. However, in the case of Seed A substrate, unlike Seed B, there was an absence of SiV^- at the wavelength of 736.6 nm. Consequently, the presence of the silicon-vacancy defect, also known as SiV^-, was identified in Seed B. SiV^- is characterized by a single silicon atom bonded to a missing carbon atom in the diamond crystal lattice.

Interestingly, both Seed A and Seed B exhibited the presence of a neutral "nitrogen-vacancy" (NV^0) with a zero-phonon line (ZPL) at a wavelength of 575 nm. Additionally, negatively charged "nitrogen-vacancy" (NV^-) centers were detected at the wavelength of 637 nm (Figure 3). These findings highlight the nuanced differences in the defect characteristics between Seed A and Seed B substrates, contributing to a deeper understanding of the crystal quality and composition in the context of epitaxial diamond growth.

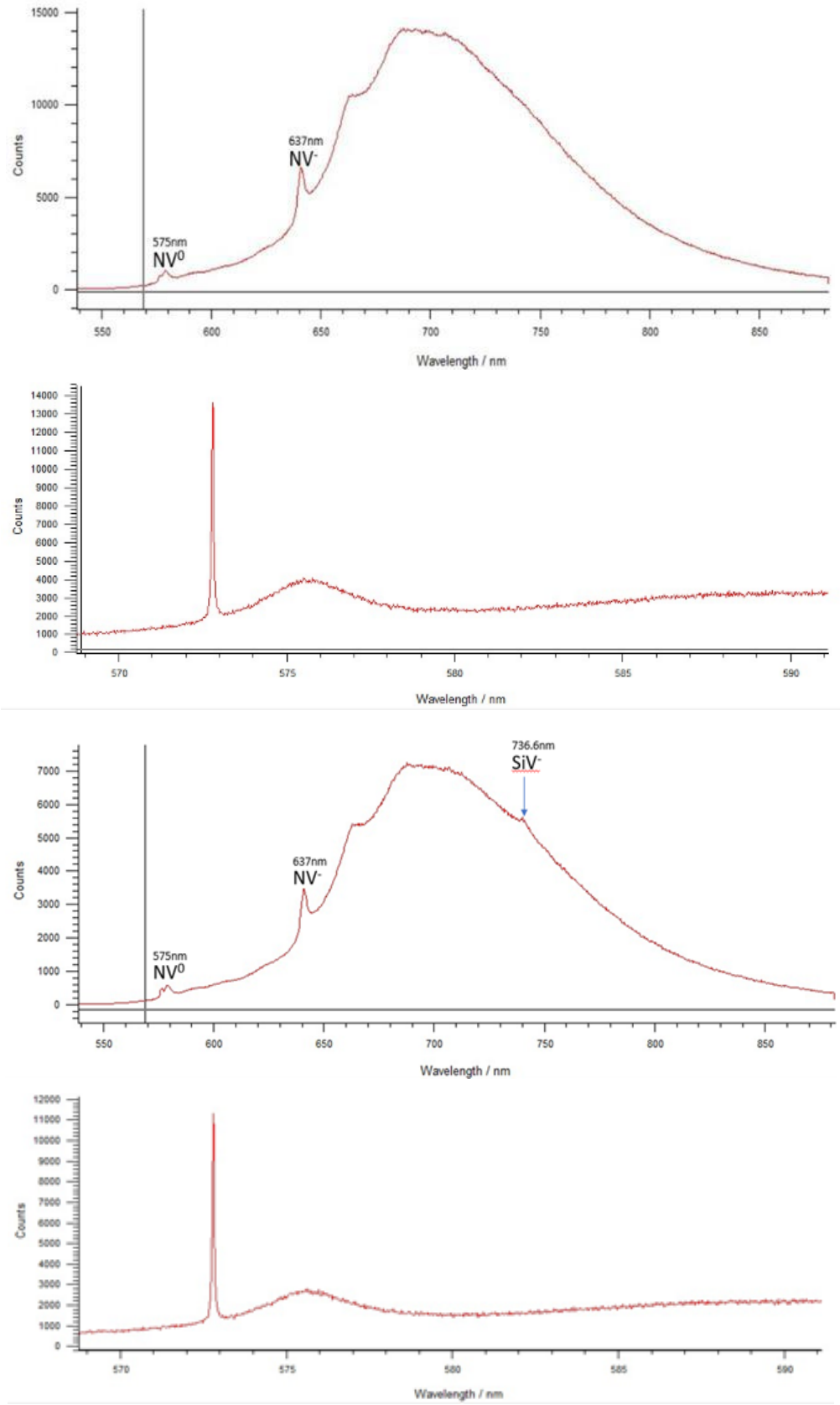

Figure 3. Seed A (top) and Seed B (below) photoluminescence spectra

Using the Microwave Plasma Enhanced Chemical Vapor Deposition (MWCVD) method, 21 pieces of 7x7x0.3 mm Seed A and Seed B were employed as substrates. For both Seed A and Seed B, a 400h growth was carried out by generating an 8% CH_4/H_2 plasma under constant microwave power and constant pressure. After the 400h growth period, Seed A exhibited an average growth of 4.23 mm, while Seed B displayed a slightly higher average growth of 4.27 mm. Notably, Seed B presented visible inclusions on the crystal surface and internal crystal defects attributed to stress. The occurrence of these defects can be attributed to the overheating of the crystal structure induced by silicon impurities, leading to stress within the crystal. As a result, despite Seed B demonstrating a higher growth rate, the compromised crystal quality, as evidenced by inclusions and defects, prompted the decision to continue subsequent growths with Seed A substrates (Figure 4). This choice was made to prioritize crystal quality over growth rate in the interest of achieving optimal results in the epitaxial diamond growth process.

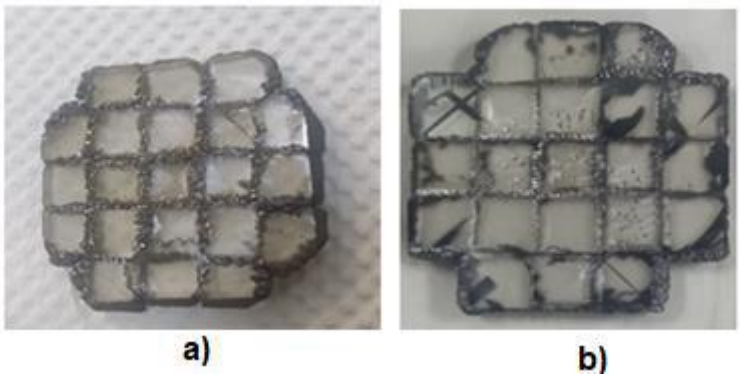

Figure 4. (a) Seed A, (b) Seed B

Diamond epilayer films were grown by introducing hydrogen and methane plasma in a controlled environment. The hydrogen gas used had a purity of 7N, while the methane gas had a purity of 6N. Throughout the growth process, the temperature, pressure, and microwave power were maintained at constant levels, and a total growth time of 400 hours was implemented. The aim was to investigate the impact of the CH_4/H_2 ratio on the diamond growth rate. Prior to the growth phase, a meticulous cleaning process was conducted for 21 substrates measuring 7x7x0.3 mm. These substrates, oriented at 100, were then strategically placed on the molybdenum surface using a method referred to as mosaic growth in the literature (Wang, 2019). This technique ensures that there are no gaps between each substrate.

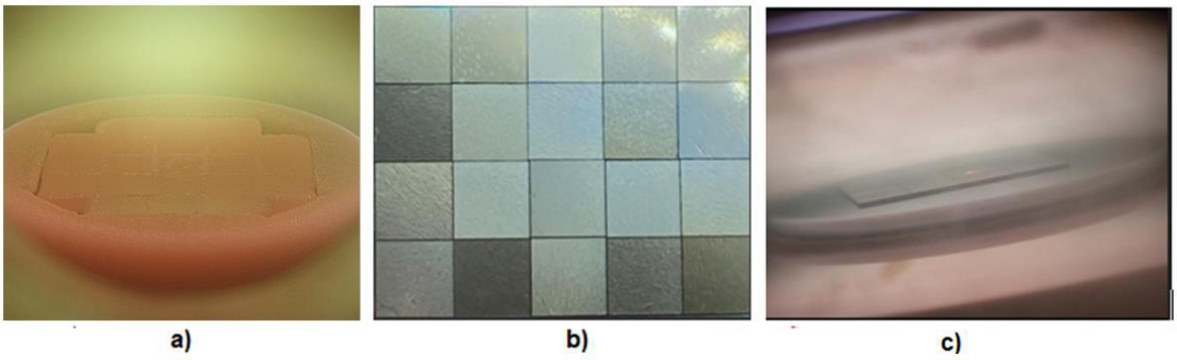

Figure 5. (a) Plasma formation during growth (b) Mosaic growth in reactor (c) Substrate sample

The growth rates resulting from three distinct 400-hour growth experiments on the MWCVD device are detailed in Table 1 below. The growth rate was calculated using the Formula 1:

$$Growth\ rate = \frac{Average\ Thickness - Substrate\ Thickness}{Growth\ Time} \quad (1)$$

This systematic approach allowed for a comprehensive examination of the relationship between the CH_4/H_2 ratio and the resulting diamond growth rates, providing valuable insights for further understanding the epitaxial diamond growth process.

Table 1. Growth rates of diamond films grown with different CH_4/H_2 ratios

No	CH_4/H_2 Rate	Average Thickness (mm)	Substrate Thickness (mm)	Growth Time (h)	Growth Rate (µm/h)
1	6	3.89	0.3	400	8.975
2	8	4.23	0.3	400	9.825
3	10	5.02	0.3	400	11.80

The investigation revealed that as the CH_4/H_2 ratios increase, the growth rate of diamond films also increases. However, a notable observation emerged from the growth with a 10% CH_4/H_2 ratio, where issues related to color quality in the diamond films and the occurrence of numerous polycrystalline diamond growths on the substrate edges were noted (Figure 6). The most optimal growth, considering color quality, was achieved using a 6% CH_4/H_2 ratio. However, it was deemed insufficient for the company's profit policy. As a result, future studies will be directed towards enhancing both the quality and growth rate of diamond films, with a specific focus on growth with an 8% CH_4/H_2 ratio. This balanced ratio is expected to offer a favorable

compromise between color quality and profitability. Furthermore, the impact of flow rates on the growth rate is illustrated in the graph below (Figure 7). This data will be instrumental in refining the growth parameters for achieving the desired balance between growth rate and diamond film quality in the ongoing research and development efforts.

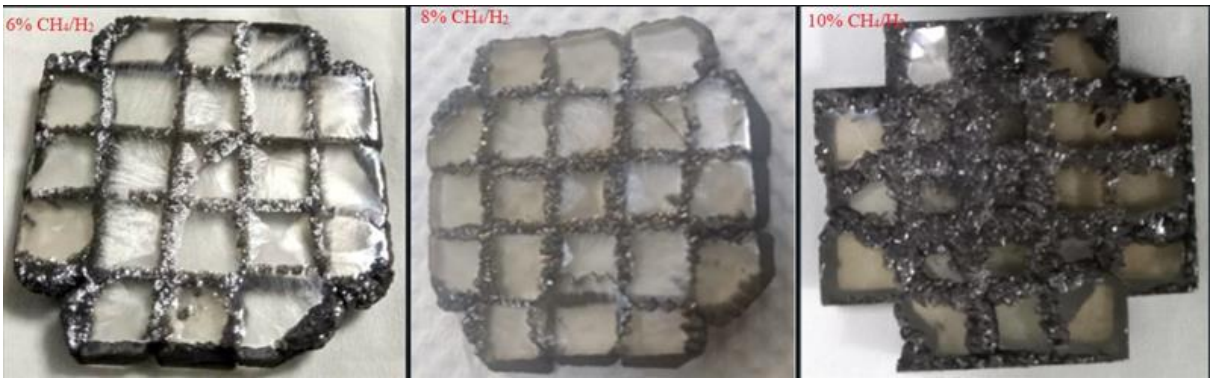

Figure 6. Growth result of diamond films grown with different CH_4/H_2ratios

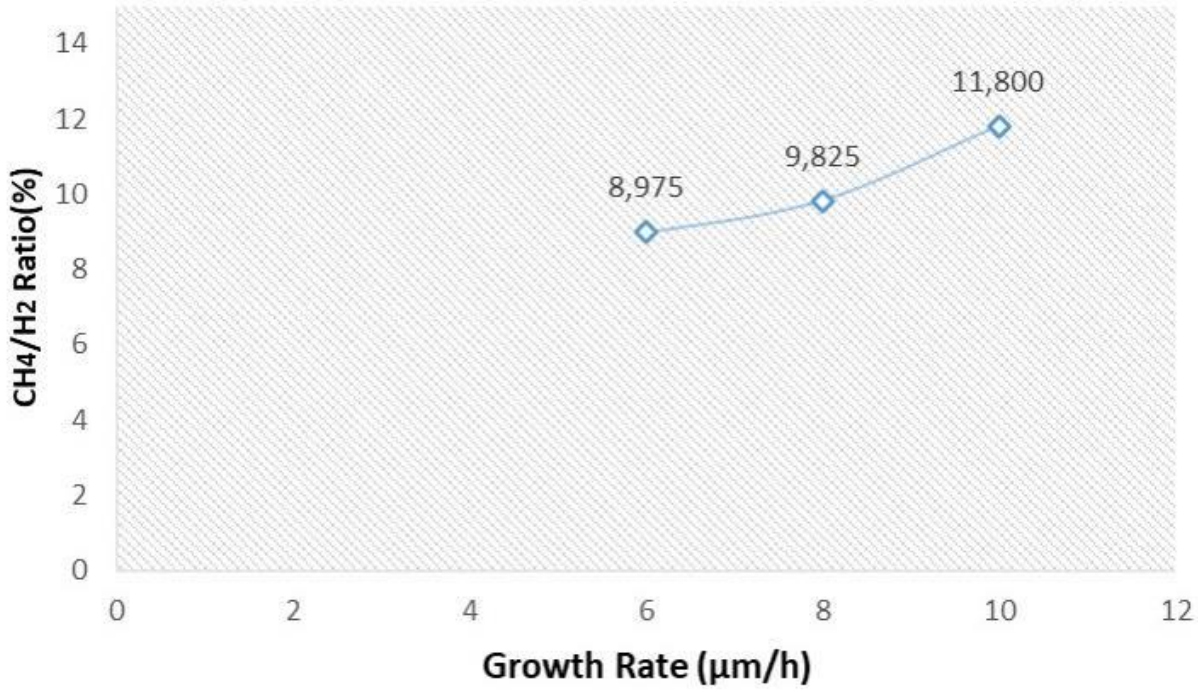

Figure 7. Effect of flow rates on growth rate

CONCLUSION

Within the scope of this study, two separate companies, SEED A and SEED B, provided different substrates produced with different production methods. SEED A uses ion implantation and levitation, a technique commonly used in semiconductor manufacturing. Using the Microwave Plasma Enhanced Chemical Vapor Deposition (MWCVD) method, 21 pieces of

7x7x0.3 mm Seed A and Seed B were used as substrates. For both Seed A and Seed B, 400h of growth was achieved by generating 8% CH_4/H_2 plasma under constant microwave power and constant pressure. After the 400h growth period, Seed A exhibited an average growth of 4.23 mm, while Seed B exhibited an average growth of 4.23 mm.

Seed B, in particular, presented visible inclusions on the crystal surface and internal crystal defects attributed to stress. The appearance of these defects can be attributed to the overheating of the crystal structure caused by silicon impurities, leading to stress within the crystal. According to the variable gas ratio at constant values of temperature, pressure and microwave power, 970oC, 135 Torr and 5700W, respectively, the growth rate of diamond films increases as the CH_4/H_2 ratio increases. However, as a result of the growth with 10% CH_4/H_2 ratio, color quality in the diamond films and a lot of polycrystalline diamond growth on the lower substrate edges were observed. the best magnification in terms of color quality was obtained by using a 6% CH_4/H_2 ratio. Although Seed B exhibited a higher growth rate, growth was continued with Seed A in subsequent growths due to defects in growth due to residues. This choice was made to prioritize crystal quality over growth rate to achieve the best results in the epitaxial diamond growth process. In this study, for the first time in the literature, the molybdenum surface was coated with AlTiN and TiN using the "physical vapor deposition (PVD)" method, homogeneously with the PVD method and the coating thickness was applied as 5 micrometers.

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