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Investigation of depositing large area uniform diamond films in multi-mode MPCVD chamber

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ABSTRACT

In this work, diamond films were deposited in a 10 kW, 2450 MHz MPCVD apparatus, of which the chamber allows a multi-mode microwave electric field to be overlapped and high microwave power to be employed. The two primary modes of TM_{01} and TM_{02} overlap around the substrate and generate a large scale plasma ball which ensures the deposition of large area diamond films. The deposition temperature across the substrate was primarily investigated in order to deposit uniform diamond films in the multi-mode chamber. And the optical emission spectra, scanning electron microscope and Raman were used to characterize the diamond films. The results showed that higher microwave power should be selected to generate large plasma ball and obtain needed temperature uniformity for a given deposition pressure. And the temperature variation was decreased obviously when the substrate holder was improved. With the optimized parameter and the improved stage configuration, the diamond thin films deposited on $\Phi = 80$ mm silicon wafers obtained excellent uniformity in morphology, thickness and quality. And the results of investigating growth rate further confirm that the improved substrate holder and the employment of high microwave power are useful to achieve uniform diamond films with large area and high deposition rate.

1. Introduction

Diamond possesses a large number of unrivalled physical and chemical properties such as extreme hardness, high thermal conductivity, wide band gap, high optical transparency and excellent chemical stability etc. [1,2]. In regard of that, diamond is attractive for many applications in the fields of optics, machinery, electronics, medicine and so on [3–7]. And during the last two decades, the chemical vapor deposition (CVD) apparatus and processes for diamond film deposition were established and developed, and the microwave plasma chemical vapor deposition (MPCVD) attracted more attention due to the advantage of the production of an electrodeless discharge and an associated high density plasma as well as the synthesis of high quality diamond [8].

A large number of researchers have carried out experiments to deposit and research diamond films with various types of MPCVD apparatuses. Man et al. have deposited diamond film with 50 mm in diameter using CH_3OH/H_2 as a gas source in a 5 kW cylindrical type MPCVD (2450 MHz) and researched the optical characterization [9]. Zuo et al. have investigated the uniformity and quality of freestanding diamond films in a 2450 MHz quartz bell type MPCVD [10]. King et al. have researched the technology of scaling 2450 MHz quartz bell type MPCVD reactor to a larger size by employing 915 MHz microwave energy [11]. The diameter of the substrates was up to 200 mm in the scaled up MPCVD reactor. Tachibana et al. have deposited large area diamond films on $\Phi = 150$ mm substrates in a 60 kW MPCVD (915 MHz) and investigated α parameters, the CVD conditions for morphology control and the diamond films texture etc. in detail [12–14]. Recently, Li et al. have designed a novel MPCVD reactor for diamond film deposition and the preliminary experiments showed that the density of plasma and the quality of the diamond films deposited in the apparatus were high [15]. It is clear that several efforts have been made to prepare diamond films in various types of MPCVD apparatuses in order to increase the uniformity and the area of diamond films. However, the apparatus with single mode chamber, such as the cylindrical type MPCVD (2450 MHz), the quartz bell type MPCVD (2450 MHz) and the quartz tube type MPCVD, is difficult to be deposited with large area diamond films because of the scale limitation of the chamber. Therefore the investigations of large area uniform diamond films deposited by the MPCVD apparatus which can increase the area of diamond films are necessary and important to satisfy the needs of various applications.

In this paper, uniform diamond films with 80 mm in diameter were deposited in a 10 kW, 2450 MHz MPCVD system. The quality, uniformity and surface morphology of the deposited diamond films were primarily investigated from the aspect of controlling the substrate temperature uniformity. And an improved substrate holder was designed in

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the investigation to increase the uniformity of diamond films. Numerous data accumulated from the experiments, on the one hand, ascertain the feasibility of depositing large area diamond films. On the other hand, the new reactor is used as a guide to explore the deposition conditions in a larger reactor with higher microwave power and plasma density. The preliminary experimental results obtained by the 10 kW, 2450 MHz MPCVD apparatus are described.

2. Experimental details

2.1. Description of the MPCVD apparatus

All the diamond films were deposited on mono-crystalline silicon substrates in a 10 kW, 2450 MHz MPCVD reactor. And the scale of the MPCVD apparatus is smaller than that with multi-mode chamber using 915 MHz microwave as microwave power. The inside dimensions of the chamber are approximately 420 mm in diameter, and the cooling substrate holder (Cu) with 230 mm in diameter is located at the center of the reactor which can accommodate a substrate up to 120 mm in diameter. The height of the reactor versus the reactor radius is around 95 mm, and the dimensions of the "top hat" are around 106 mm in diameter and 62 mm in height. The cross-section view of the MPCVD reactor used in this experiment is shown in Fig. 1(a), and the modeling results of the microwave electric field distribution inside the chamber are shown in Fig. 1(b). As shown in Fig. 1(a), the antenna with a cone-shaped inner conductor introduces microwave energy into the chamber through the ring-shaped quartz window which is located underneath the cooling substrate holder and far from the plasma reducing the damage to window from plasma such as overheating and etching. Meanwhile the ring-shaped quartz window also possesses the function of achieving a high vacuum in the deposition chamber.

It is worth to notice that the chamber is a multi-mode resonant cavity allowing two primary microwave modes of TM_{01} and TM_{02} to overlap and to excite a large scale plasma ball. As shown in Fig. 1(b), standing microwave interference patterns are formed in the reactor. It also can be observed from the modeling result that along the radial directions, the number of the standing microwave electric field patterns is two which confirms that the dominant resonant modes of microwave in the reactor are TM_{01} and TM_{02}. The design of the reactor makes the electric field satisfy the condition that the weak area of TM_{01} is just the strong area of TM_{02}. The plasma ball generated at that condition is large enough to ensure the deposition area of CVD diamond film [15]. Compared to the deposition area in MPCVD with single-mode cavity, the size of plasma ball is larger and can be up to 150 mm in diameter. Besides that all the components of the resonant cavity, coaxial antenna, substrate holder etc. are water-cooled which also ensures the inputting of high microwave power.

2.2. Experiment and characterization

Prior to diamond film deposition, the vacuum of the reactor chamber was evacuated to less than 1.0 Pa. The silicon wafers with thickness of 400 ± 20 μm were scratched with 0.5 μm diamond powder before deposition, and all the wafers were ultrasonically cleaned with acetone, methanol, and deionized water for 3–5 min respectively following the scratching. For the process gas, the mixture of methane (CH_4, purity of 99.99%) and hydrogen (H_2, purity of 99.99%) was introduced into the chamber with mass flow meter (MFM) controller. The carbon concentration in the experiment was kept at 0.6–5.0% and the total input gas flow rate was kept at 303.5–310.0 sccm. The deposition pressure was adjusted by pumping throttle valves. During the experiments of diamond film deposition, the plasma was generated initially with 1 kW of power using the precursor gas of H_2. Once ignited the microwave power, the input gas and pressure were increased to the desired operating conditions. The plasma ball with two microwave modes could be kept by adjusting microwave power and chamber pressure. The substrate temperature was monitored by a two-color infrared radiation thermometer through observation windows and controlled by the balance between microwave plasma heating and water-cooling since no separate heating was applied to the substrate holder.

Optical emission spectra were used to research the main particles in the plasma ball. Scanning electron microscopy (SEM, JSM-5510LV Japan) was used to characterize the surface morphology of the diamond films, and the quality of which was evaluated by Raman spectroscopy (Raman, DXR, U.S.A.) with Ar laser operated at 514.5 nm.

3. Results and discussion

In CVD diamond film deposition, substrate temperature is considered as one of the most important factors in the synthesis of diamond films [12,16,17]. And many factors, including microwave power, deposition pressure and substrate holder design etc., have an influence on substrate temperature. Fig. 2 shows substrate temperature as a relationship of microwave power and deposition pressure with the gas flows of 300 sccm hydrogen and 3.5 sccm methane. The plasma ball generated at each microwave power and deposition pressure can cover a wafer with a diameter of 100 mm. As shown in Fig. 2, for a given deposition pressure, the substrate temperature increases with increasing microwave power. Meanwhile for a given microwave power, the substrate temperature also increases with increasing deposition pressure. Thus, at a substrate temperature of 850 °C for example, the microwave

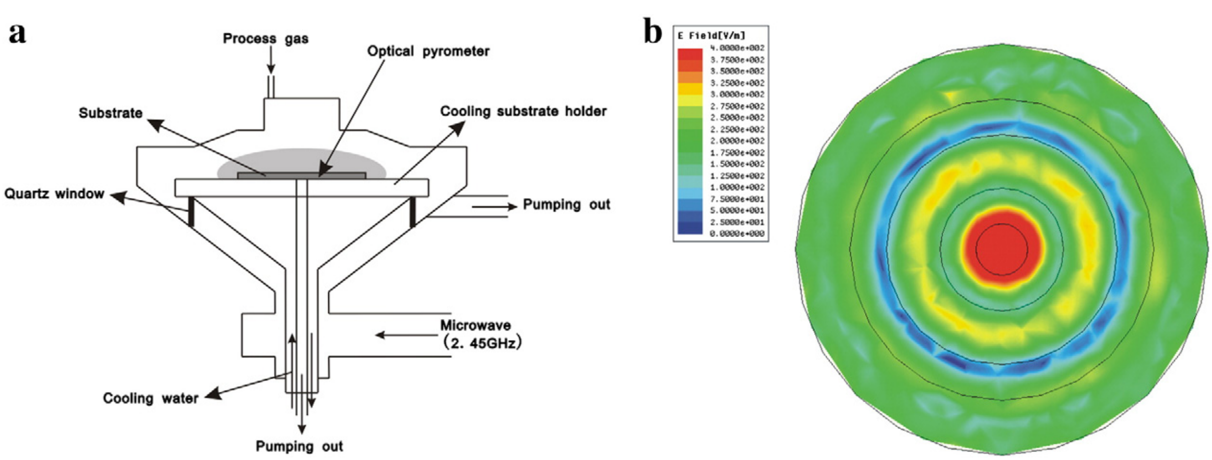

Fig 1. Schematic of the 10 kW MPCVD reactor used in the experiment (a) and the modeling result of electric field in the reactor (b).