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July 28, 2005

American Insitute of Physics, Conference Proceedings,
RF2005 workshop Kalamata Greece

Investigation of the Millimeter-Wave Plasma Assisted CVD Reactor

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Abstract. A polycrystalline diamond grown by the chemical vapor deposition (CVD) technique is recognized as a unique material for high power electronic devices owing to unrivaled combination of properties such as ultra-low microwave absorption, high thermal conductivity, high mechanical strength and chemical stability. Microwave vacuum windows for modern high power sources and transmission lines operating at the megawatt power level require high quality diamond disks with a diameter of several centimeters and a thickness of a few millimeters. The microwave plasma-assisted CVD technique exploited today to produce such disks has low deposition rate, which limits the availability of large size diamond disk windows. High-electron-density plasma generated by the millimeter-wave power was suggested for enhanced-growth-rate CVD. In this paper a general description of the 30 GHz gyrotron-based facility is presented. The output radiation of the gyrotron is converted into four wave-beams. Free localized plasma in the shape of a disk with diameter much larger than the wavelength of the radiation is formed in the intersection area of the wave-beams. The results of investigation of the plasma parameters, as well as the first results of diamond film deposition are presented. The prospects for commercially producing vacuum window diamond disks for high power microwave devices at much lower costs and processing times than currently available are outlined.

Keywords: Plasma, Chemical vapor deposition, Millimeter-waves, Gyrotron
PACS: 81.15 Gh

INTRODUCTION

Recently, the microwave plasma-assisted chemical vapour deposition process (MPACVD) has received wide acceptance [1]. Since the contact of electrode-free plasma with the walls of the reactor can be excluded, the working gas mixture retains high purity making possible the growth of high quality films. At present the majority of microwave CVD reactors operate at a frequency of 2.45 GHz. The use of microwave power at this frequency is mainly explained by the availability of microwave sources (magnetrons) with power levels up to 5 - 6 kW. On the other hand, the use of microwaves with large wavelengths (λ = 12,25 cm), makes it possible to create a fairly uniform plasma with dimensions (about a half wavelength) sufficiently large for producing diamond films up to several centimeters in diameter. The main shortcoming of these reactors is the low growth rate of high quality polycrystalline diamond (of order of 1-2 microns per hour) which results in high costs and long processing times of thick diamond disks required for high power applications.

The rate of growth can be increased with an increase in the concentration of chemically active particles, the most important being hydrogen atoms which are produced in plasma as a result of collisions of electrons with gas molecules. A group from the Institute of Applied Physics (IAP), Nizhny Novgorod, Russia proposed to use microwave power at higher frequency for the MPA CVD process [2] in order to increase the electron density and microwave power absorbed per unit volume of plasma. Generalized results of modeling the discharges maintained by microwaves at two different frequencies are presented in Table 1. The concentration of hydrogen atoms, the most important characteristic in the process of diamond film growth, is an order of magnitude higher at 30 GHz compared with the concentration produced using conventional 2.45GHz microwaves.

TABLE 1. Main Characteristics of Plasmas Maintained by Microwaves of Different Frequencies.

Frequency, GHz	**Electron Density, cm^{-3}**	**Maximal Concentration of Hydrogen Atoms, cm^{-3}**	**Concentration of Hydrogen Atoms Near Substrate, cm^{-3}**
2.45	$5\cdot10^{11}$	$2\cdot10^{16}$	$6\cdot10^{14}$
30	$5\cdot10^{12}$	$5\cdot10^{17}$	10^{16}

The concept of forming a plasma layer maintained by the millimeter-wave power is based on the experimental and theoretical results of the study into gas discharge in intersecting wave beams [3]. The results of previous research as well as acquired experience provided the background for the development of the millimeter-wave plasma assisted CVD technique.

MILLIMETER-WAVE PLASMA ASSISTED CVD REACTOR

The development of a plasma CVD reactor, which uses the millimeter-wave power, faces two major problems.

1. *Generation of a stationary plasma layer of high uniformity by application of an electromagnetic wave with the wavelength (λ=10 mm) much smaller than the area of deposition (diameter of area about 80 mm).* The plasma layer in the reactor under development consists of gas discharge plasma maintained by intersecting converging wave-beams. The plasma is sustained in the localized region of the enhanced field arising within the intersection of the beams. The dimension and shape of the plasma layer can be controlled by varying the area of intersection and its geometry.
2. *Transport of high millimeter-wave power to the reactor and forming wave-beams with performance characteristics needed for maintaining the stationary plasma configuration.* Since the millimeter-wave power of about 10 kW is to be applied to the reactor, it is evident that the problem has to be solved by methods of quasi-optical antenna synthesis.

A schematic of the MPA CVD system based on the use of a 30 GHz 10 kW gyrotron is shown in Fig.1. The mode converter (2) transforms the operating H_{02} mode of the gyrotron (1) into a Gaussian wave beam and directs it to the oversized corrugated waveguide (3). The wave beam is divided into four identical wave beams using a divider (4). A unit of four mirrors placed at 90° degrees to each other directs

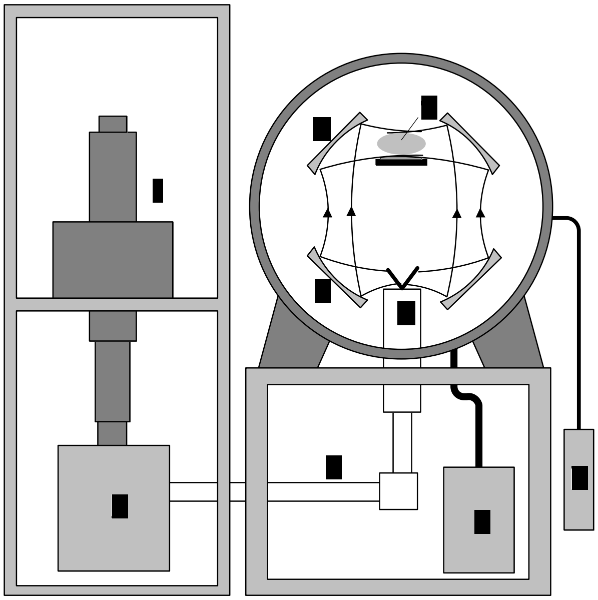


FIGURE 1. Schematic of the MPA CVD system based on use of the 30 GHz 10 kW gyrotron. 1 – gyrotron, 2 – mode converter, 3 – waveguide feeder, 4 – wave-beam divider, 5 – set of reflectors, 6 – set of focusing mirrors, 7 – gas mixture supply, 8 – pumping out system, 9 – a region near substrate to be occupied by microwave plasma

the wave beams to four mirrors (5) which reflect the wave beams to four focusing mirrors(6).

A gas discharge (9) arises in the strong electromagnetic field resulting from the intersecting of wave beams near the substrate. The profile of the electromagnetic field intensity in the intersection area depends on the polarization of the electric field in intersecting beams. The plane of polarization in the wave-beam reflected from the focusing mirror can be precisely controlled by making the reflecting surface a specified corrugated profile. In this way, the parameters of plasma in the gas discharge and the shape of the plasma layer can be controlled.

The system also includes a gas mixture supply (7), a pump out system, a set of power supplies, a computer-base control system, a cooling system, and a set of diagnostics which are not shown in Fig.1.

FIRST RESULTS OF DIAMOND FILM DEPOSITION

The operation of the MPA CVD system has been tested at various millimeter-wave power levels applied to the chamber filled with Ar/H_2 gas mixtures at different pressures. Shown in Fig. 2 is a photograph of the microwave discharge above the substrate when the pressure of the Ar/H_2 gas mixture is 150 Torr. Under the effect of the plasma the substrate heats up to significant temperatures (600...900 ºC), and the change in the gas density on the discharge periphery influences the discharge shape. As seen in the figure, the discharge has a disc shape with a diameter equal to the substrate diameter and a thickness of 2 cm. Such a discharge shape makes it possible to achieve sufficiently high energy input into the discharge plasma.

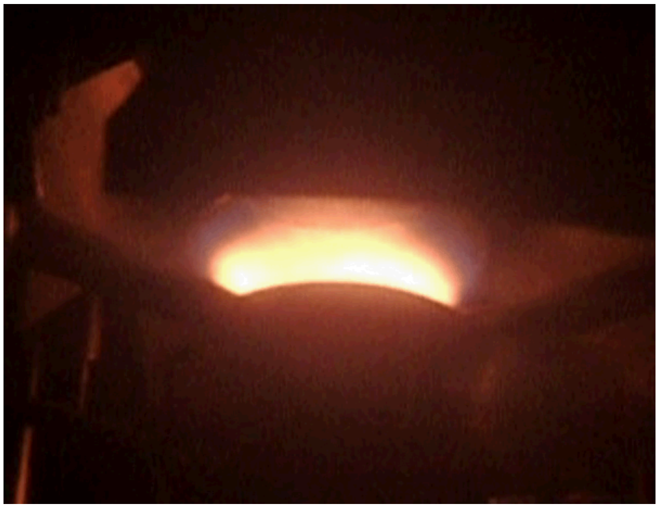


FIGURE 2. Photograph of the discharge above the substrate when the pressure of the Ar/H_2 gas mixture is 150 Torr

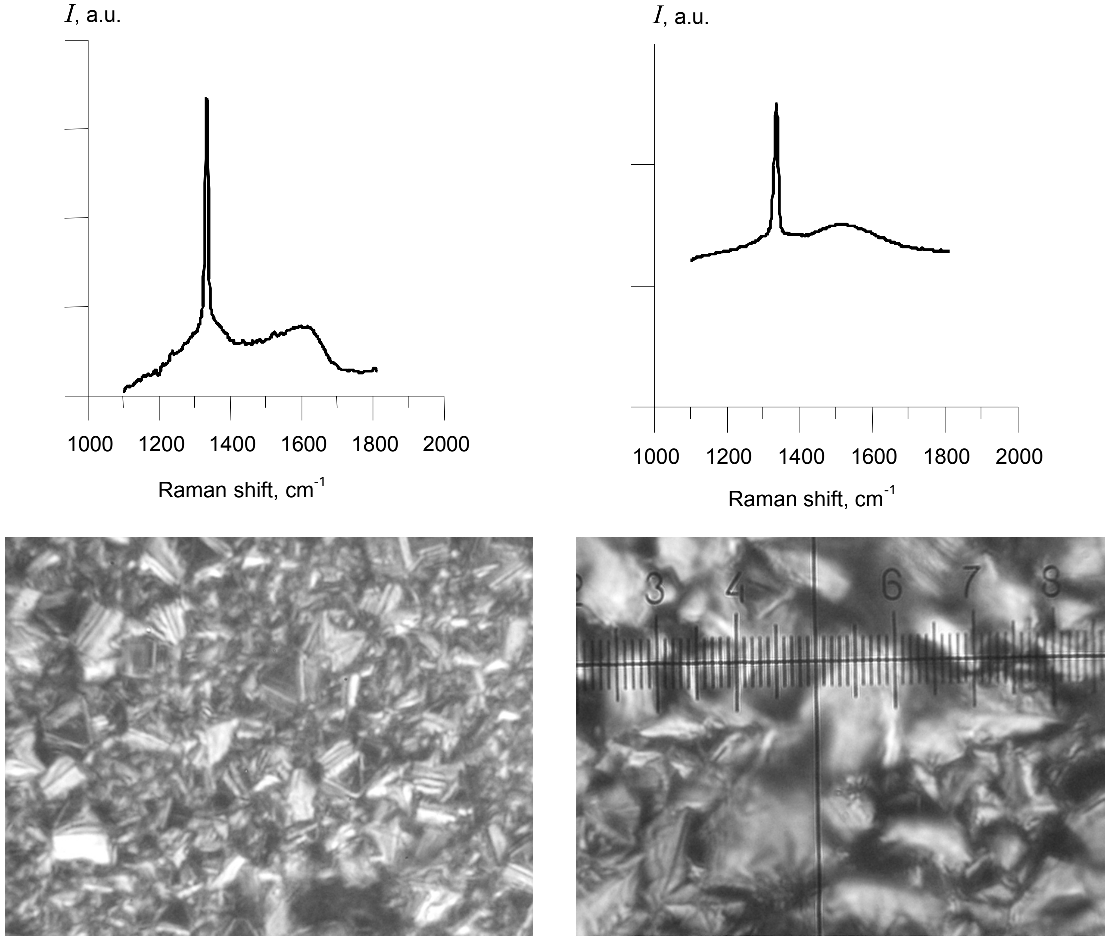
The investigation of diamond film deposition on Silicon substrates was carried out in the gas mixture of $Ar/H_2/CH_4$. The pressure and composition of gas mixture, gas flow rates, microwave powers and substrate temperature were varied.

The quality of the deposited diamond films was studied using Raman scattering spectra. Since different carbon structures have different Raman scattering spectra, this method makes it possible to assess the film quality based on such features as diamond to graphite phase ratio, the "quality" of the diamond phase (determined by the diamond-phase scattering peak width), and the amount of defects in the crystalline lattice. The morphology of the film surface (orientation of crystals, their size and shape) can also provide information about the film deposition process.

In order make an objective comparison between the diamond film deposition processes in the 2.45 and 30 GHz CVD reactors, a series of experiments were carried out keeping the same gas mixture composition, pressure, gas flow rate, substrate temperature and the input microwave power. The $Ar/H_2/CH_4$ gas mixture was used in these experiments.

Fig. 3 shows examples of Raman scattering spectra of diamond films deposited in the 30 GHz and 2.45 GHz CVD reactors at microwave power levels of about 6 kW, deposition temperature of 820°C, and gas pressure of 200 Torr. Also shown in Fig. 3 is the microphotograph of the film surfaces obtained with an atomic force microscope.

It should be noted that in the 2.45 GHz CVD reactor, the diamond film deposition was carried out during 8 hours at an average deposition rate of 0.6 $mg/(hr\cdot cm^2)$, whereas in the 30 GHz reactor the films were grown for 1 hour at an average deposition rate of 3 $mg/(hr\cdot cm^2)$. As observed in Fig. 3, the ratio of the diamond peak (1332 cm^{-1}) to broad band at (1520÷1600) cm^{-1}, commonly interpreted as amorphous or disordered carbon, is no less in the film grown in the 30 GHz reactor despite the growth rate in the 30GHz reactor being five times larger than in the 2.45 GHz reactor.



a) *b)*

FIGURE 3. Raman scattering spectra and microphotographs of the surface of diamond films grown in CVD reactors operating at 30 GHz, deposition time is 1 hr (a), and 2.45 GHz, deposition time is 8 hr (b).

In addition, the microstructure of the film grown at 30 GHz is more uniform and this may lead to enhanced mechanical properties of the deposited material.

It is known that the nucleation step takes a rather long time at the initial stage of diamond film deposition. It was found that when the diamond film was deposited in the 2.45 GHz CVD reactor, the diamond phase grew as separate nuclei during the first hour and did not form a continuous film. The results of experiments demonstrate that in the 30 GHz reactor, the deposition rate is higher, and the nucleation step takes less time. It is also known that the average growth rate of diamond films increases with an increase in the CVD process time. Therefore, an even more objective comparison between the processes of diamond film deposition in two reactors operated at the different frequencies could be made if the deposition times were equal.

One might expect that a further increase in the diamond film growth rate can be obtained in the 30 GHz reactor with an increase in the CVD process time.

CONCLUSION

1. The millimeter-wave plasma assisted CVD reactor based on the 30 GHz 10 kW gyrotron has been designed and constructed. The output radiation of the gyrotron is transformed into four Gaussian wave-beams. The free localized plasma layer in the reactor is formed in the region of the wave-beam intersection.
2. The gyrotron operating characteristics and gas condition in the reactor were found for steady-state gas discharge plasmas.
3. Thin diamond films were grown in the 30 and 2.45 GHz reactors for identical parameters of the gas mixture. The growth rate of diamond films in the 30 GHz reactor was at least 5 times larger than the growth rate in the 2.54 GHz reactor.

Acknowledgments

This work was performed under the auspices of the US Department of Energy by UC, LLNL under Contract W-7405-Eng-48 and funded under the IPP program, project LLNL-T2-224-RU, as well funded by the contract № 40.031.1.1.1183 of the Russian Ministry of Science and Education.

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