Investigation of microwave discharge in cavity reactor excited in the $\text{TM}_{013}$ mode

M.A. Lobaev, S.A. Bogdanov, D.B. Radishev, A.L. Vikharev, A.M. Gorbachev

Institute of Applied Physics RAS, Nizhny Novgorod, Russia
OUTLINE

1. Introduction
2. Experimental setup
3. Numerical model
4. Experimental results
   4.1 Microwave power density (MPWD)
   4.2 Atomic hydrogen density
   4.3 Gas temperature
5. Conclusion
My report is devoted to investigation of microwave discharge in cavity reactor excited in the $\text{TM}_{013}$ mode.

We investigated the discharge in hydrogen with a small amount of methane about 1 percent. The discharge was investigated in the wide pressure range from 80 to 350 Torr. Such a discharge is used to produce diamond films from the gas phase (CVD diamonds). First, I will say a few words about CVD diamond. Then I will talk about reactors which produce CVD diamond. The main part of the reactor is a microwave resonator. Microwave power density in plasma is used for comparison different types of reactors. We propose a method for determining the microwave power density which allows carrying out a comparison of different reactors correctly. Then I will show how you can use the method. We also investigated how other parameters are changed in such a wide pressure range.

Here you can see examples of poly and single crystal diamond obtained in our laboratory. Pictures were taken in a different scale. Disk size 75 mm. Single crystal size 3 by 3 mm. The use of diamond is due to its unique properties. Polycrystalline disks are used for the output windows of high-power microwave devices. Single crystals are used for particle detectors. Doping single crystals are used to create powerful diodes and transistors.
Here you can see the main types of CVD reactors which are used for deposition of diamond films. The main part of the reactor is a resonator. Usually use TM modes with different numbers. Plasma is created under quartz bell jar. Typically plasma has the following parameters. Gas mixture hydrogen with methane content (1 – 5%). Pressure 80 – 300 Torr. Microwave power 1 - 6 kW. Gas temperature 2800 – 3300 K. Electron temperature 1 – 2 eV. Substrate temperature 800 – 1200 K. At this temperature, the deposition of diamond. Distribution of electric fields is different for these reactors. Therefore the plasma parameters vary too. Experimental results for different reactors difficult to compare.

The growth rate of a diamond is determined by the Goodwin’s formula. Growth rate of diamond growth is proportional to the concentration of hydrogen and methyl radical near the substrate. Methyl radical occurs in the following reaction. Calculations show that the main parameter that determines the value of the concentration of atomic hydrogen is microwave power density. Increasing the power density also increases the concentration of atomic hydrogen. The microwave power density is defined as the ratio of the absorbed microwave power to the plasma volume. This parameter is used to compare the different reactors. Different groups define it differently.

Sometimes used a certain level of luminosity. Sometimes used bright luminous core of the plasma. Sometimes used of argon glow. Argon is added for diagnostics. How to determine the amount of plasma?
We propose a method for determination of plasma volume, which to us seems to be more correct than the other methods. The method is as follows:

1. Photograph the discharge through the filter Hα. Use photos for determine the level of intensity at which begins to affect background illumination.
2. Using a numerical model to compare distributions of microwave power density and Hα
3. Determine plasma volume using Hα distribution.

CVD reactor used in our experiment is similar in design to Michigan State University reactor. The discharge was created in a cylindrical resonator, excited in the $\text{TM}_{013}$ at frequency 2.45 ГГц. Our setup allows investigating the parameters of the plasma in the pressure range 50 – 350 Topp when the power of magnetron up to 5 kW. To observe the optical emission spectra, we used a such spectrometer. The experiments were performed both in pure hydrogen, and in hydrogen with a small methane content (1%). For the experiments the following conditions were chosen: the power was 2.3 kW, a flow of hydrogen was 300 sccm, the gas pressure was varied in the range of 80-350 Torr.
For photos of the plasma we used a screen. Image was made by a digital camera. To avoid glare the photos were made in total darkness. For each experiment, we made two photos: with and without filter Hα. We used the data obtained directly from the camera in RAW. When converting from RAW to jpg nonlinear transformation occurs. We used software that makes only a linear transformation. The linearity of the measurements was checked by several test shots taken with different exposures (from few to tens of seconds), and is estimated to be no more than a few percent.

Here are shown photographs of a discharge in hydrogen with small amount (1%) methane made without a filter and with a filter. With increasing pressure, the plasma volume decreases. From the photos you can see that the distribution αH slightly wider than the distribution of the total luminosity. This is particularly noticeable at high gas pressure. Photos taken at different exposures. At higher pressure the main contribution to the glow discharge produce hydrocarbon radicals.

Для нахождения связи между областью, где светит Hα и областью где происходит поглощение энергии, мы использовали численную модель разряда. Модель можно условно разбить на следующие блоки.
По сравнению с предыдущей модель была дополнена расчетом функции распределения электронов. До этого мы использовали аппроксимации констант, взятые из других работ, где рассчитывалась функция распределения.

сл.11
Здесь показано сравнение расчетных распределений с экспериментальными. В расчете мы синтезировали фотографию $H\alpha$. Как видно расчетные распределения $H\alpha$ хорошо совпадает с экспериментальным. Как видно из графиков характерный масштаб распределения $H\alpha$ совпадает с характерным масштабом распределения энерговклада. Поэтому распределение $H\alpha$ можно использовать для определения объема плазмы.

сл.12
Здесь показано сравнение энерговкладов полученное разными методами. The discharge boundary is determined by the intensity taken at level of 15% of the maximum value. This level was chosen to reliably “tune out” of the noise associated with background illumination. Из графика видно, что энерговклад измеренный по $H\alpha$ меньше чем измеренный по интегральной светимость. Это особенно заметно при более высоких давлениях. При более высоких давлениях основной вклад в интегральное свечение дают углеводородные радикала СН и С2. При больших содержаниях метана разница между этими кривыми будет значительно больше. Энерговклад измеренный в чистом водороде меньше чем в водород метановой смеси. Это связано с тем что при переходе к чистому водороду происходит смена основного
ион в разряде с C2H2+ на H3+. Меняется ионизацияционно рекомбинационный баланс и объем плазмы в чистом водороде становится больше.
сл.13
We also investigated some over impotent parameters of discharge. We used well-known actinometric method. This method is based on the comparison of the radiation intensities of atomic hydrogen and an actinometer a small admixture of a chemically inert gas to the working mixture. This method yields adequate results if the following conditions are satisfied for both atomic hydrogen and the actinometer.
1. The radiating levels should be excited by electron impact from the ground state.
2. The threshold excitation energies of atomic hydrogen and the actinometer should be close to one another.
3. The excited levels should be quenched via the known mechanism.
To determine the atomic hydrogen density, we chose the Ar (2p9, 8115 Å, 13.08 eV) line and the Hγ (n = 5, 4340 Å, 13.06 eV) line. Our previous investigation showed that this couple of lines satisfied to all of this conditions.
сл.14
Концентрация атомарного водорода растет с ростом давления. Добавка метана не приводит к росту концентрации атомарного водорода.
The gas temperature is an important parameter for optimization of diamond films deposition, because influences the rate of plasma chemical reaction. To measure the gas temperature we used the emission from the $^3D_g \rightarrow ^3P_u$ transition (Swan band) of C$_2$ radical. Radiative lifetime of $^3D_g$ level is greater than the collisions frequency so the distribution of emission intensity from rotational sublevels of $^3D_g$ electronic level should be well described by Boltzmann distribution with the rotational temperature close to gas kinetic temperature.

The “tail” of the spectrum has an alternating lines from P and R branches with significantly different quantum numbers, and these lines are well resolved even with a low-resolution devices. Due to this, even the small changes of rotational temperature produces a notable change in the “tail” of the spectrum, which can significantly increase the accuracy of measurement of rotational temperature.

Температура газа меняется в диапазоне 2800 – 3400 К. Gas temperature limitation caused by the H$_2$ thermal-dissociation reaction (energy cost 4.8 eV): H$_2$+M$\rightarrow$H+H+M.

We have carried out investigation of microwave discharge in a resonator excited at the TM$_{013}$ mode in a wide range of gas pressures (80-350 Torr). Such discharges are used for chemical vapor deposition of diamond films.
We have measured microwave power density, concentration of atomic hydrogen and gas temperature. The microwave power density varied from 50 to 500 W/cm$^3$ when pressure increases from 80 to 350 Torr.

We propose the method for determining the microwave power density. Plasma volume is determined by the photos of the discharge made through H$\alpha$ line filter. The discharge boundary is determined by the intensity taken at level of 15% of the maximum value. The proposed method seems to be more appropriate in order to compare operation regimes of different CVD reactors.
Introduction

Polycrystalline diamond

- UV and particle detectors
- Field effect transistors
- High-power Schottky diodes
- UV LED
- etc.

Single crystal diamond

- RF window
- Heat sink
- etc.

Unique properties of diamond

- Thermal conductivity: 20 (W/cm·K)
- Dielectric losses $\tan \delta$: $10^{-6} – 10^{-5}$
- Band gap: 5.45 (eV)
- Breakdown electric field: 10 (MV/cm)
2.45 GHz CVD reactors

MSU

ASTEX

Aixtron

Plassys

Plasma parameters

Gas mixture: hydrogen with methane content (1 – 5%)
Pressure: 80 – 300 Torr
Microwave power: 1 - 6 kW
Gas temperature: 2800 – 3300 K
Electron temperature: 1 – 2 eV
Substrate temperature: 800 – 1200 K

Introduction

**Growth rate and defects density [*]**

\[
G \propto \frac{[\text{CH}_3]_{\text{sur}}[\text{H}]_{\text{sur}}}{3 \cdot 10^{15} \text{ cm}^{-3} + [\text{H}]_{\text{sur}}}
\]

\[
X_{\text{def}} \propto \frac{G}{[\text{H}]^2_{\text{sur}}}
\]

\[CH_4 + H \leftrightarrow CH_3 + H_2\]

Microwave power density (MWPD) = Absorbed power / Plasma volume

How to determine plasma volume correctly?

The method for determining the microwave power density

1. Photograph the discharge through the H\(\alpha\) filter. Use photos for determine the level of intensity at which begins to affect background illumination.
2. Using a numerical model to compare distributions of microwave power density and H\(\alpha\)
3. Determine plasma volume using H\(\alpha\) distribution.
Experimental setup

1 - cylindrical resonator, 2 - coaxial waveguide, 3 - rectangular waveguide, 4 - circulator with matching load, 5 - magnetron unit, 6 - microwave discharge, 7 - quartz bell jar, 8 - buffer vacuum volume, 9 - evacuation system, 10 - gas supply system, 11 - magnetron power supply, 12 - control computer, 13 - diagnostic window, 14 - Horiba Jobin Yvon FHR-1000 monochromator, 15 - photoelectric multiplier, 16 - digital oscillograph, 17 - computer, 18 - monochromator control unit
Experimental setup

Measurement scheme (top view)

1 - resonator wall, 2 - microwave discharge, 3 - objective lens, 4 - white screen, 5 - DSLR camera, 6 - concave lens, 7 - optical fiber.

Photo of the discharge was made with a digital SLR camera. The software used produces only a linear transformation of the intensity for each pixel of the original RAW file for the photo.
Images of the plasma obtained on the paper screen

Without filter

\[ p = 80 \text{ Torr} \]
\[ p = 145 \text{ Torr} \]
\[ p = 350 \text{ Torr} \]

With H\(\alpha\) filter

\[ p = 80 \text{ Torr} \]
\[ p = 145 \text{ Torr} \]
\[ p = 350 \text{ Torr} \]

Absorbed power 2.3 kW, methane content 1\%
Numerical model [*]

**Electromagnetic module.** Calculation of electromagnetic fields in the reactor by FDTD method with plasma introduced via the conduction currents.

**Plasma module.** Calculation of plasma density in the discharge.

**Gas dynamics module.** Calculation of the density, temperature and velocity of the neutral gas.

**Atomic hydrogen module.** Calculation of atomic hydrogen density using balance equation considering diffusion and transfer.

**EEDF module.** We used Monte Carlo method. The calculation of the distribution function took into account the impact of the gas temperature, the vibrational excitation and degree of dissociation of hydrogen. The constants of reactions involving electrons were calculated using the obtained distribution function.

Numerical model

Axial distributions

Radial distributions

$p = 80$ Torr

$p = 145$ Torr

$p = 350$ Torr

1 – MWPD, 2 – Hα image – model, 3 - Hα image - experiment
Plasma volume is determined by the photos of the discharge made through Hα line filter. The discharge boundary is determined by the intensity taken at level of 15% of the maximum value. This level was chosen to reliably “tune out” of the noise associated with background illumination.

Absorbed power 2.3 kW
Experimental results. Atomic hydrogen density

Actinometric method [*]

1. The radiating levels should be excited by electron impact from the ground state.

2. The threshold excitation energies of atomic hydrogen and the actinometer should be close to one another.

3. The excited levels should be quenched via the known mechanism.

\[
\frac{\partial N_i^*}{\partial t} = k_{ei} N_e N_i - k_{qi} N N_i^* - \frac{N_i^*}{\tau_i} \quad \Rightarrow \quad I_i = N_i^* A_i \frac{hc}{\lambda_i} \propto N_i \quad \Rightarrow \quad \frac{N_1}{N_2} = \frac{I_1}{I_2} \cdot \frac{k_{e2}}{k_{e1}} \cdot \left[ \frac{k_{q1} N + 1/\tau_1}{k_{q2} N + 1/\tau_2} \right] \cdot \text{const}
\]

\[
\frac{N_1}{N_2} = \frac{I_1}{I_2} \cdot \text{const}
\]

To determine the atomic hydrogen density, we chose the Ar (2p9, 8115 Å, 13.08 eV) line and the Hγ (n = 5, 4340 Å, 13.06 eV) line [**]


Experimental results. Atomic hydrogen density

![Graph showing the variation of \( \frac{I(H\gamma)}{I(Ar)} \) with pressure (Torr) for pure hydrogen and pure hydrogen with 1% methane.](image)
Experimental results. Gas temperature

Rotation structure of $C_2$ (transition $d^3\Pi_g \rightarrow a^3\Pi_u$)

Radiative lifetime of $d^3\Pi_g$ level is greater than the collisions frequency so the distribution of emission intensity from rotational sublevels of $d^3\Pi_g$ electronic level should be well described by Boltzmann distribution with the rotational temperature close to gas kinetic temperature.

The “tail” of the spectrum has an alternating lines from P and R branches with significantly different quantum numbers, and these lines are well resolved even with a low-resolution devices. Due to this, even the small changes of rotational temperature produces a notable change in the “tail” of the spectrum, which can significantly increase the accuracy of measurement of rotational temperature.
Gas temperature limitation caused by the $\text{H}_2$ thermal-dissociation reaction (energy cost 4.8 eV): $\text{H}_2 + \text{M} \rightarrow \text{H} + \text{H} + \text{M}$.
We have carried out investigation of microwave discharge in a resonator excited at the $\text{TM}_{013}$ mode in a wide range of gas pressures (80-350 Torr). Such discharges are used for chemical vapor deposition of diamond films. We have measured microwave power density, concentration of atomic hydrogen and gas temperature. The microwave power density varied from 50 to 500 W/cm$^3$ when pressure increases from 80 to 350 Torr. We propose the method for determining the microwave power density. Plasma volume is determined by the photos of the discharge made through H$\alpha$ line filter. The discharge boundary is determined by the intensity taken at level of 15% of the maximum value. The proposed method seems to be more appropriate in order to compare operation regimes of different CVD reactors.