

Development of dielectric barrier discharge plasma processing apparatus for mass spectrometry and thin film deposition

Abhijit Majumdar^{a)} and Rainer Hippler

Institut für Physik, Ernst-Moritz-Arndt-Universität Greifswald, Felix-Hausdorff-Strasse 6, 17489 Greifswald, Germany

(Received 20 March 2007; accepted 31 May 2007; published online 3 July 2007)

Cost effective and a very simple dielectric barrier discharge plasma processing apparatus for thin film deposition and mass spectroscopic analysis of organic gas mixture has been described. The interesting features of the apparatus are the construction of the dielectric electrodes made of aluminum oxide or alumina (Al_2O_3) and glass and the generation of high ignition voltage from the spark plug transformer taken from car. Metal capacitor is introduced in between ground and oscilloscope to measure the executing power during the discharge and the average electron density in the plasma region. The organic polymer films have been deposited on Si (100) substrate using several organic gas compositions. The experimental setup provides a unique drainage system from the reaction chamber controlled by a membrane pump to suck out and remove the poisonous gases or residuals (cyanogens, H-CN, CH_xNH_2 , etc.) which have been produced during the discharge of CH_4/N_2 mixture. © 2007 American Institute of Physics. [DOI: 10.1063/1.2751408]

I. INTRODUCTION

If an ac voltage is applied to one of the electrode with both covered by a dielectric layer, a discharge will appear in the gas gap which is the so-called dielectric barrier discharge (DBD) or barrier discharge.¹⁻⁴ Near atmospheric pressure DBDs are of great interest for application in, e.g., fundamental gas chemistry, sterilization, surface activation, and modification or thin film deposition.³⁻⁷ The numbers of industrial plasma technological and chemical applications of DBD discharge are widely taken into part in the utilization of greenhouse gases (CO_2 and CH_4).⁴ It would be the easiest way to affect the chemical kinetics by varying the chemical composition of the feeding gas mixture during the barrier discharge plasma process. The development of a new process based on this discharge needs a clear understanding of plasma and discharge physics and chemistry. At present time much attention is paid to the development and the modification of barrier discharge processes, since the understanding is necessary for the development of industrial reactors.⁸ The measurement of electrical power of barrier discharge plasma has been described by Wagner *et al.*⁹

In this article we describe a simple, less time consuming to operate, and inexpensive DBD plasma processing and thin film deposition apparatus. The major contribution to this work is the probe measurement technique which helps us to estimate (or model) the average electron density and effective electrical power in the plasma region during discharge. The air gap between two electrodes is modified by introducing variable Teflon [polytetrafluoroethylene (PTFE)] insulating plates depending on the experimental requirement. The

chances of short circuiting (during high voltage discharge experiment) is removed with the improvement of proper grounding and earthing system.

II. APPARATUS

The schematic diagram of DBD apparatus is shown in Fig. 1. The DBD setup is the assembly of several components which are the following: (A) reaction chamber and electrodes configuration, (B) electrical inputs, (C) gas flow system, (D) pumping system, (E) probe measurement, and (F) spectrograph.

A. Reaction chamber and electrode configuration

The reaction chamber is made of stainless steel. The inner dimensions of the chamber are height of 12.3 cm, length of 18.0 cm, and width of 15.0 cm, yielding a chamber volume of 3.32 dm³. The two electrodes are made from Ag plates with a length of 8.3 cm, width of 3.3 cm, and thickness of 0.15 cm. The Ag plate is placed in a rectangular shape Plesiglass holder or container and both the Ag electrodes are covered by dielectrics: the upper (powered) electrode is covered with aluminum oxide ($\epsilon \sim 10$) and the lower (grounded) electrode with a glass plate ($\epsilon \sim 3.8$) (shown in Fig. 2). The air gap between two electrodes is variable, depending on the experimental condition and it is insulated by Teflon (PTFE) insulation. The dimensions of the Teflon insulator are width of 4 cm, length of 1.9 cm, and thickness is variable from 0.5 to 5 mm. The position of the substrate is on glass. The upper electrode is connected to a homebuilt high voltage power supply, while the lower electrode is grounded.

From Fig. 3, we can see the three-dimensional configuration and position of the DBD electrodes as placed in reactor chamber. To deposit film on glass, we have used the glass

^{a)} Author to whom correspondence should be addressed; electronic mail: majumdar@physik.uni-greifswald.de

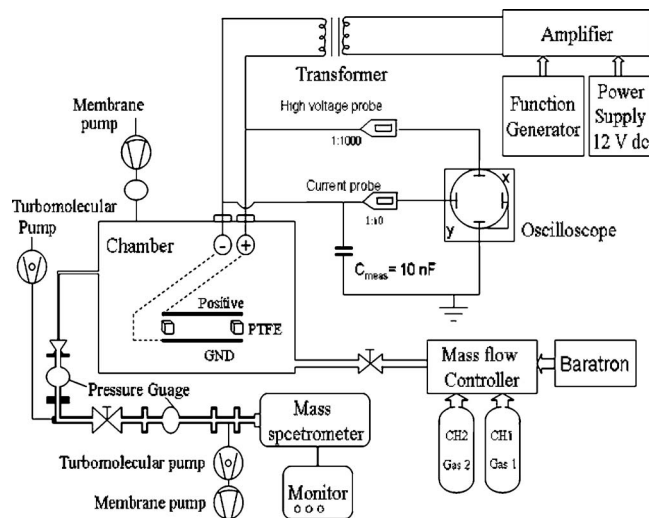


FIG. 1. Schematic diagram of dielectric barrier discharge apparatus.

as dummy substrate and put it on the glass substrate. In another case to deposit on Si (100), we put a small piece of Si (100) wafer on the glass substrate. Whenever dummy substrate is placed on the ground electrode for deposition, the distance between two electrodes is maintained by changing the thickness of the Teflon insulation. In both the cases, we found the homogeneous plasma with our eyes open outside of the chamber.

B. Pumping system

The chamber is pumped by a membrane pump down to a base pressure of about 10 mbars. The experiments were performed at a pressure of 250–400 mbars and with varying different gas ratios. Membrane vacuum pump (Pfeiffer, GmbH, Germany) is used to evacuate the reaction chamber up to 1 mbar. Turbomolecular pump (Pfeiffer, TCP 121) is introduced at the end of the capillary tube to create the pressure gradient in between the chamber and mass spectrometer end. Gas composition of stable reaction products was only detected by a mass spectrometer (Balzers QMS 200) pumped by a turbomolecular pump (Pfeiffer TSU 062H) to a base pressure of about 1×10^{-8} mbar.

C. Gas flow system

Gas flow system consists of (i) baratron (MKS Instruments, USA) (ii) multiple mass flow controller (MKS Instruments, USA), and (iii) gas cylinder (CH_4 , Ar, N_2 , H_2 , He, etc.). Out of the four channels of mass flow controller, only two channels are used in the prospective experiments. Chan-

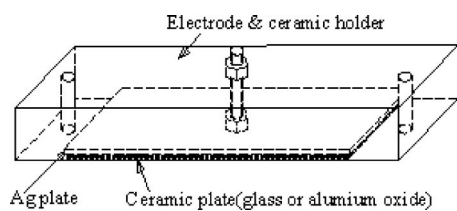


FIG. 2. Three-dimensional view of single electrode used in barrier discharge.

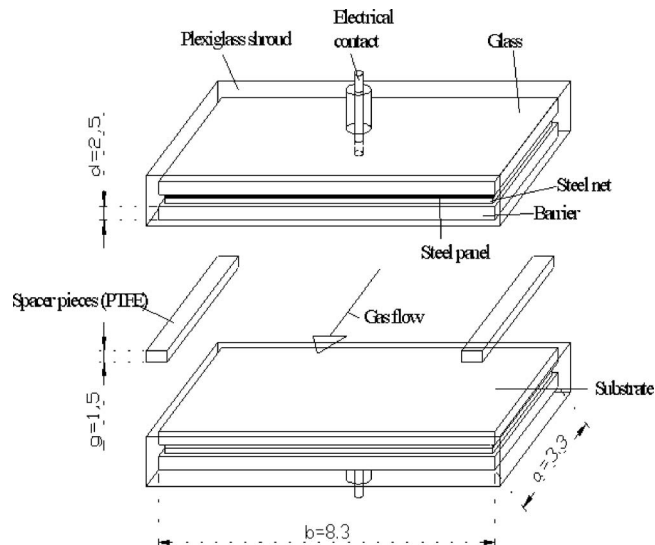


FIG. 3. Three-dimensional view and position of the two barrier electrodes.

nel 1 is fixed with methane gas flow, and channel 2 is variable with different gas flow arrangements as shown in Fig. 1. The pressure inside the plasma chamber was controlled by two gas flow controllers for methane and nitrogen or other gases and by an adjustable needle valve between the chamber and the membrane pump. Once the chamber is filled up with the reactive gas mixtures up to the desired pressure, then it has been isolated from the surrounding during the experiment.

D. Electrical inputs

The electrical system is accompanied by (i) power supply, (ii) function generator, (iii) amplifier (HURRICANE, GmbH, Germany), and (iv) spark plug transformer. The power supply of 12 V dc is used to bias the audio amplifier for the threshold potential. The function generator or frequency generator delivers a sinusoidal output that is fed into an audio amplifier. The amplifier can be operated at up to 500 W. The output from the amplifier is fed into a spark plug transformer. This spark plug transformer is taken from a car which helps to ignite the high threshold voltage for the discharge. The phase part of the transformer connected to the positive electrode (upper electrode, Al_2O_3) and other part is connected to earth to the 220 main line. The lower electrode is connected to the ground through the metal capacitor. The whole experimental setup is ultimately connected with proper earthing. To get the barrier discharge, it needs a threshold potential of ~ 4 kV, depending on the properties of the organic gas mixture. The electrical system offered the range from 4 kV (peak to peak) to 15 kV with the frequency range from 2 to 7.5 kHz for the stable dielectric barrier discharge.

E. Probe measurement

The probe measurement is one of the most interesting parts of the DBD apparatus. The probe system is an assembly of (i) high voltage (Tektronix P16015 A, 1000 \times , 3.0 pF, 100 M Ω) and current probe (Tektronix P6103, 50 MHz,

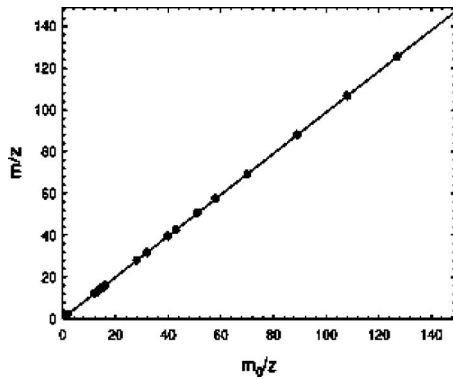


FIG. 4. The displayed mass number m/z vs the correct mass number m_0/z . The solid line is a least-squares fit yielding $m/z=0.2711+0.9853m_0/z$.

10 M Ω , 13.2 pF), (ii) metal capacitor (10 nF), and (iii) oscilloscope (Tektronix TDS 220, 100 MHz, 1 Gsample/s, USA). Usually microdischarges are of nanosecond duration, uniformly distributed over the dielectric surface. The dielectric electrode can be considered as capacitor plate. To characterize the overall discharge behavior, an equivalent circuit can be used. The equivalent circuit configuration and electrical power calculation (by Lissajous figure) have been described by Wagner *et al.*⁹ In order to calculate the mean electron density, we consider the charge accumulated at the capacitor plates: total charge accumulated=capacitance \times maximum voltage or

$$Q = CU_{\max} = \left(\frac{\epsilon A}{d} \right) V,$$

where ϵ is the permittivity of the medium (8.85×10^{-12} F/m) and A and d area and distance between DBD plates, respectively. U_{\max} is the peak to peak maximum applied voltage.

For the dimension and better understanding, we put $\epsilon = F/m$ (only unit), applied voltage= V , distance between two plates= d (m), area of the DBD plates= A (m²),

$$Q = \left(\frac{\epsilon A}{d} \right) V \text{ [F] [m}^{-1}\text{] [m}^2\text{] [m}^{-1}\text{] [V]}.$$

We know that farad=coulomb/voltage= C/V and coulomb (C)=ampere \times second= IS ,

$$1 \text{ electron charge} = -1.6 \times 10^{-19} \text{ C}$$

and

$$1 \text{ C} = \frac{1}{1.6 \times 10^{-19}} e^- = 0.625 \times 10^{19} e^-.$$

Putting the value of $1 \text{ C} = 6.25 \times 10^{18} e^-$ and $\epsilon = 8.85 \times 10^{-12}$ F/m, we get that the total charge accumulated on the capacitor plate is

$$Q = (6.25 \times 10^{18})(8.85 \times 10^{-12}) \times \left(\frac{A}{d} \right) V \text{ [V}^{-1}\text{] [m}^{-1}\text{] [m}^2\text{] [m}^{-1}\text{] [V] [e}^-]$$

or

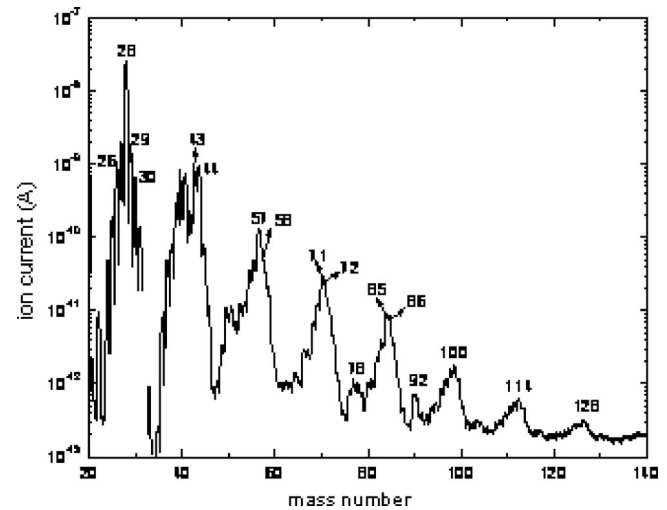


FIG. 5. Difference mass spectrum with and without plasma in the mass range $m/z=20-140$ for a CH_4/Ar (1:2) gas mixture.

$$Q = (5.531 \times 10^7) \times \left(\frac{A}{d} \right) V \text{ [V}^{-1}\text{] [m}^{-1}\text{] [m}^2\text{] [m}^{-1}\text{] [V] [e}^-]$$

or

$$Q = (5.531 \times 10^7) \left(\frac{A}{d} \right) V e^-.$$

A typical discharge takes about $\tau \approx 10$ ns (transit time) and is repeated at a frequency f . Calculating the reaction volume V from the volume between the DBD plates, we can estimate the average electron density n_e (or which is also referred as volume charge density) as

$$n_e \approx \frac{Q}{V} \tau f \approx \left\{ \frac{(5.531 \times 10^7) [(A/d)V]}{V} \right\} \times 10^{-9} \times f \frac{e^-}{\text{cm}^3}$$

or

$$n_e \approx (5.531 \times 10^{-2}) \left(\frac{AV}{dV} \right) f \frac{e^-}{\text{cm}^3}.$$

Now, putting the value of volume (V), area (A), distance between two electrodes (d), applied voltage (V), and the frequency (f) in the above equation, we can estimate the average electron density of the DBD plasma.

F. Spectrograph

The mass spectrometer (Balzers QMS 200) is connected to the reaction (plasma) chamber through a capillary tube of length of 103 cm and inner diameter of 0.01 cm. A pressure of 10^{-2} mbar at the entrance to the mass spectrometer is maintained during the experiments with the help of a second turbomolecular pump (Balzers 071P). The gas composition of stable reaction products was only detected by a mass spectrometer (Balzers QMS 200) pumped by a turbomolecular pump (Pfeiffer TSU 062H) to a base pressure of about 1×10^{-8} mbar.

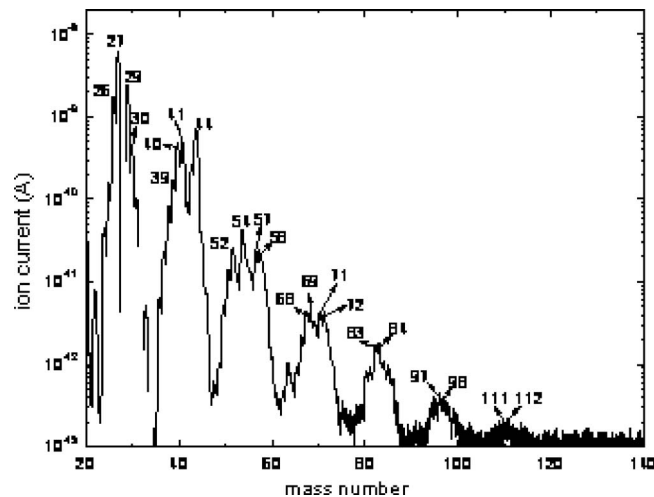


FIG. 6. Difference mass spectrum with and without plasma in the mass range $m/z=20-140$ for a CH_4/N_2 (1:2) gas mixture.

III. OPERATION CONDITIONS AND CALIBRATION

The reaction chamber has to be evacuated by a membrane pump up to 1 mbar before any experiment. After filling up the chamber with the gas mixture up to 300–500 mbars as per requirement, it is isolated from the surroundings by using needle valve arrangement. A capillary tube with diameter of 0.1 mm is connected with the mass spectrometer to the reaction chamber. A second turbomolecular pump (Balzers 071P) is used to create the pressure gradient in between chamber and the mass spectrometer. The water flow should be on during the discharge to cool down the mass spectrometer filament and the high voltage transformer coil and amplifier system. The grounding and earthing should be checked properly before discharge. Once the discharge is on the voltage can be varied from 4 to 15 kV (peak to peak) and the frequency can be varied from 2 to 7.5 kHz.

To accurately determine the mass number of the detected species, we have carried out a mass calibration employing H_2 , CH_4 , N_2 , Ar, Xe, and SF_6 gases. The results are shown in Fig. 4, where the displayed mass number m/z is plotted versus the correct mass number m_0/z . The solid line is a least-squares fit yielding $m/z=0.2711+0.9853m_0/z$. Small deviations amounting to up to about one mass number around 100 amu are noted and have been taken into account in the assignment of the observed species. To compare the hydrogen (H_2) and methane (CH_4) signals, relative sensitivity calibration was performed with 300 mbars of either CH_4/Ar or CH_4/N_2 gas mixture (mixing ratio of 1:2) and with 20–100 mbars of H_2 .

IV. RESULTS

The experimental results have been shown here which were performed at 10.5 kV (peak to peak) voltage and at a frequency of 5.5 kHz. The electrical power under these conditions was 5 W. The mass spectrum results of DBD plasma are shown here in Figs. 5 and 6. From Fig. 5, we can see the difference mass spectrum of CH_4/Ar gas mixture, for mass number from $m/z=20-140$ ranges, on a logarithmic scale. It

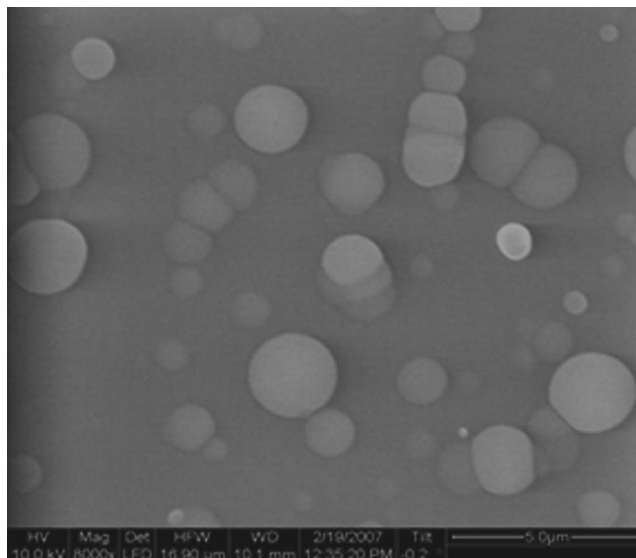


FIG. 7. SEM image of deposited SiC film by CH_4/Ar (1:2) DBD plasma.

has been obtained by subtracting the data without plasma from those obtained with plasma. The main reaction scheme is the production of H_2 by fragmentation of CH_4 , but also production of higher order hydrocarbon molecules including the formation of different functional groups. The broad prominent peaks are composed of several individual peaks attributed to C_nH_m molecules with n up to 9 and $m=2n+2$. The most prominent peaks hence approximately differ by $m/z=14$ from each other. Evidently, one CH_2 radical is adding up in consecutive reactions, and in consequence the spectrum becomes periodic. Figure 6 shows the difference spectrum in the mass range $m/z=20-140$ on a logarithmic scale. Again, the broad prominent peaks, each composed of several individual peaks, are attributed to C_nH_m molecules with n up to 8. In addition, consumption of N_2 is noted which may give rise to the formation of HCN ($m/z=27$) and its CN ($m/z=26$) fragment. As the $m/z=26$ and 27 peaks overlap with C_2H_2 and C_2H_3 , respectively, no unambiguous identification is possible. However, the detailed results and the analytical reaction schemes are not discussed here.

The deposited films were investigated by several analytical techniques but presently only a scanning electron microscopy (SEM) result has been shown here. Figure 7 displays the SEM picture of the diffused amorphous carbon cluster on Si (100) wafer deposited by $\text{CH}_4:\text{Ar}$ (1:2) gas mixture DBD plasma.

ACKNOWLEDGMENTS

The authors are thankful to Dr. J.F. Behnke, Dr. Hartmut Steffen, Axel Knuth, Daniel Köpp, and Jana Kredl for the help in building up the experimental setup. Part of this work was supported by the Deutsche Forschungsgemeinschaft (DFG) through Sonderforschungsbereich SFB/TR24 *Fundamentals of Complex Plasmas* and by The International Max Planck Research School (IMPRS) “Bounded Plasmas.” Thanks are due to Dr. Ralf Schneider and Dr. K. Matyash, Max-Planck Institute, Greifswald, Germany, for several discussion. The authors are also thankful to Professor S. R.

Bhattacharyya, SINP, Kolkata, India, for SEM measurement and several discussions.

- ¹D. Braun, U. Küchler, and G. Pietsch, *J. Phys. D* **24**, 564 (1991).
- ²D. Braun, V. Gibalov, and G. Pietsch, *Plasma Sources Sci. Technol.* **1**, 166 (1992).
- ³A. Sonnenfeld, T. M. Tun, L. Zajickova, K. V. Kozlov, H.-E. Wagner, J. F. Behnke, and R. Hippler, *Plasma Polym.* **6**, 237 (2002).
- ⁴K. V. Kozlov, P. Michel, and H.-E. Wagner, *Czech. J. Phys.* **48**, No. 10 (1998).
- ⁵U. Kogelschatz, and J. Salge, in *Low Pressure Plasma Physics*, edited by R. Hippler, S. Pfau, M. Schmidt, and K. H. Schoenbach (Wiley-VCH, Weinheim, 2001), p. 331.
- ⁶V. G. Samoilovich, V. Gibalov, and K. V. Kozlov, in *Physical Chemistry of the Barrier Discharge*, edited by J. P. F. Conrads and F. Leipold (DVS-Verlag, Düsseldorf, 1997).
- ⁷J. R. Roth, P. P.-Y. Tsai, and L. C. Wadsworth, U.S. Patent No. 5,403, 453 (4 April 1995).
- ⁸C. J. Liu, B. Xue, B. Eliasson, F. He, Y. Li, and G. H. Xu, *Plasma Chem. Plasma Process.* **21**, 301 (2001).
- ⁹H.-E. Wagner, R. Brandenburg, K. V. Kozlov, A. Sonnenfeld, P. Michel, and J. F. Behnke, *Vacuum* **71**, 417 (2003).