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PECVD of carbon by inverted fireballs: From sputtering, bias enhanced nucleation to deposition

P. Knoll [a], J. Reynvaan [a], M. Mayer [a], S. Surnev [a], P. Geistlinger [a], K. Krenn [b], K. Ettinger [b], C. Prietl [a], A. Hohenau [a], J. Gruenwald [a,1], B. Kunert [c], R. Resel [c]

[a] Institute of Physics, University of Graz, Universitätsplatz 5, A-8010 Graz, Austria
[b] Institute of Earth Sciences, University of Graz, Universitätsplatz 2, A-8010 Graz, Austria
[c] Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria

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ABSTRACT

The novel method of so called "inverted fireballs" is employed to different surface processes important in carbon deposition. This new approach of PECVD offers the possibility to influence and vary the reactive plasma in a wide range. Details of the experimental setup required for a stable inverted fireball are presented and the advantages and limits of this novel method are discussed. Sputtering of carbon films, nucleation of carbon with negative biased substrate and growth of nano-diamonds are outlined together with characterizations by means of SEM, EDX, Raman, XRD and XPS. Also an ab-initio calculation of the Raman spectrum of a small diamond cluster is presented and discussed in comparison with obtained experimental results.

1. Introduction

Inverted fireballs have been introduced to plasma research by R.L.Stenzel et al. [1,2]. This plasma phenomenon occurs if a hollow grid electrode is placed into plasma, called background plasma, biased with a positive voltage against the background plasma potential. If the grid electrode has a high transparency for the electrons, and the mesh openings are not too wide compared with the Debye-length, the electrons of the background plasma are accelerated through the grid into the encapsulated volume and enhance the plasma inside the hollow grid electrode. The glow of this intensified plasma is called inverted fireball. Because of the enhanced plasma density inside the grid electrode the use for deposition in a PECVD process has been suggested [3]. Further work has developed this method; the size of the inverted fireball was increased to 1 dm^3, its shape was modeled, the stability in pure hydrogen and reactive H_2/CH_4 mixture has been demonstrated, and the pressure range required for a stable inverted fireball has been increased to 10 Pa [4,5]. First depositions of diamond like carbon with the inverted fireball method have been presented by M.Mayer et al. [6]. One advantage of the inverted fireball method for depositions is the flexibility of the plasma shape, which enables to concentrate the plasma to that part of the volume which is responsible for the surface reaction with the substrate. If the substrate within the hollow grid electrode is biased with a voltage against the surrounding plasma potential and is equipped with a heater for temperatures up to 1000 °C, the possibility for different surface reactions is further increased. Compared with other deposition methods, the inverted fireball method belongs to DC-Plasma enhanced chemical vapor deposition with a special design of the electrodes. In contrast to other methods the substrate is placed within the hollow grid anode which protects the substrate and the growth of films by direct high energy impact of positive charged ions and the strength of the plasma is given by the electron current into the hollow anode. Because of the generation of the plasma by electron impact, the free mean path of the electrons within the reaction chamber together with their kinetic energy is critical parameter which have to be considered. A natural limit of the working gas pressure by a given distance of the electrodes is controlled by the free mean path. Low pressures up to 10 Pa favor the deposition of sp^2-like carbon with all the carbon nanophases as for instance carbon nanowalls [7]. In this paper we report on the influence of a negatively biased substrate holder and on modifications to increase the pressure range up to $2 \cdot 10^3$ Pa. At

Abbreviations: PECVD, plasma enhanced chemical vapor deposition; SEM, scanning electron microscope; EDX, energy dispersive X-ray spectroscopy; XRD, X-ray diffraction; XPS, X-ray photoemission spectroscopy; BEN, bias enhanced nucleation; ND, nano-diamond; UNCD, ultra-nano-crystalline diamond.

[1] New address: INP Leibniz Institute for Plasma Science and Technology, Greifswald, Germany.

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such higher pressures we demonstrate, that nano-diamonds have been grown by the inverted fireball method at 750 °C substrate temperatures.

2. Experimental setup

The experimental setup consists of a spherical high vacuum chamber with an inner diameter of 40 cm and an upward cylindrical extension containing the filament as shown in Fig. 1. The hollow grid electrode is placed in the center of the spherical vacuum chamber and consists of a cylindrical top electrode made of a stainless steel mesh with a mesh spacing of 90 μm and a wire diameter of 20 μm. The bottom of the cylindrical cage has an isolated bottom electrode made of high temperature resistant Inconel steel serving as a substrate holder up to temperatures of 1400 K. The whole hollow grid electrode functions as a reaction chamber and can be replaced individually with tungsten gratings or molybdenum substrate holder if required. The diameter of the substrate holder has 10 cm, the distances a

and b for the three electrodes (filament, top and bottom) can be adjusted according to the working pressure. In the low pressure regime up to 10 Pa we used a = 50 cm and b = 10 cm or b = 4 cm. For the experiments with pressure of $2 \cdot 10^3$ Pa we modified the distances to a = 4 cm and b = 4 cm. In the case of the shorter distance a the cylindrical extension of the chamber is removed. The distance b between top and bottom electrodes is not very critical but should be comparable with the free mean path of the electrons; usually this distance is kept small in order to reduce the volume of the intensified plasma. The stability of the inverted fireball strongly correlates with distance a. Best results were obtained for distances a in the range from 5 to 10 times the free mean path of the electrons. Four power supplies are used for the operation: U_h will provide the heat power for the tungsten filament to keep it at a temperature of around 2000 K for proper electron emission. Usually, the filament is negatively biased against the chamber by U_f with voltages in the range of 0 to 200 V and top and bottom electrodes are positively biased against the chamber in the range of 0 to 100 V by U_t and U_b. The stability of the inverted fireball requires a constant electron emission current from the filament which was in the range of 100 mA up to 1400 mA for the experiments reported in this work. The long term stability is achieved by computer control of the temperature of the filament at a constant voltage difference between U_f and U_t. This voltage difference needs to be kept small enough to avoid multiple ionization which leads to uncontrolled discharges. A good estimate is the number of collisions of the accelerated electrons times the ionization energy of the reaction gas. The voltage of the bottom electrode influences the potential inside the cage and the shape of the fireball. In the case of the same voltage of bottom and top electrode the cage acts like a Faraday shield producing homogeneous plasma at an almost constant potential within the cage. Most of the electron discharge current flows to the top electrode and only a few milliamps reach the bottom electrode depending on the distance compared with the free mean path of electrons and ions. The strong difference between the measured current flowing through the top grating and the bottom electrode is based on the fact, that within the cage the constant potential does not accelerate electrons or ions, and the current of the electrons reaching the bottom electrode is nearly compensated by the positive ions. At the top electrode, which is highly transparent for electrons as well as for ions, the ions are accelerated away from the cage because of its positive potential against the surrounding, but the electrons are accelerated back, oscillating through the grating until they reach the metal wires of the grating. A more positive potential at the bottom electrode will accelerate the electrons to the bottom and an increase of the current at the bottom electrode is observed until nearly the whole electron current flows through the bottom electrode. Applying negative voltages to the bottom electrode will force the positive ions to the bottom electrode and a change in the sign of the bottom current can be observed with currents of a view milliamps.

The gas pressure and composition is adjusted by two vacuum pumps and mass flow controllers all controlled by computer in order to obtain stability over long time. As shown in Fig. 1 the gas inlet is placed around 45° above the substrate and the outlet to the vacuum pump below the substrate which established a gas flow over the substrate. However, in our experiments the gas flow was kept rather low (below 50 sccm) and no further influence of the kind of gas flow has been investigated. The gas composition can be varied by several flow controllers and can be measured by mass spectroscopy. This enables defined gas atmospheres with the addition of novel gases as well as of other species like nitrogen for doping purposes. Additionally, the plasma can be characterized by a Langmuir probe (Hiden ESP) and an optical spectrometer as described in the next section.

All samples shown in this work have been grown on a standard Boron doped Si (100) waver split into smaller pieces around 1 cm^2. The surface has been cleaned with a short bath in hydrofluoric acid and subsequent rinsing with distillated water.

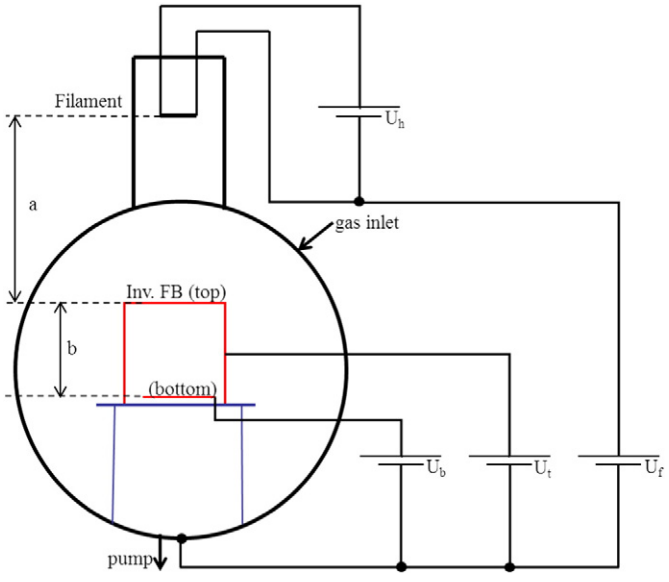

Fig. 1. Schematics of the plasma chamber.

3. Plasma characterizations

The plasma used for chemical vapor deposition should be homogeneous over the substrate area and should contain all the reactants needed for carbon growth. In order to proof these requirements we have performed Langmuir probe measurements and optical emission spectroscopy for plasma evaluation. First electrical characterizations of an inverted fireball in hydrogen plasma have shown the increased plasma density and the nearly constant plasma potential inside of the fireball [4]. In this work we concentrate on the distribution of electron and ion densities within the inverted fireball which have been determined with a standard Langmuir probe moveable through the cage. The tip of the Langmuir probe was a 10 mm long tungsten wire limiting the spatial resolution to this value. By applying different voltages against the chamber wall to this tungsten wire the I-U trace is measured. As a typical result the logarithm of the value of the measured current is plotted in Fig. 2 for hydrogen plasma at p ~1 Pa and an electron emission current of around 200 mA.

The strong minimum of the absolute value of the current around 40 V indicates the floating potential where the sign of the probe current changes. The two almost linear slopes above the floating potential and below the plasma potential around 60 V indicate the existence of two different electron temperatures typical for such plasmas induced by accelerated electrons. For a more detailed analysis a complete simulation