MICROWAVE SURFATRON SYSTEM FOR DIAMOND FILM DEPOSITIONS

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A new microwave system for plasma processing, based on a surfatron-generated plasma slab in a flowing gas, is presented. The plasma slab in a quartz tube can be used either as a downstream plasma jet for local processing or as a plasma antenna in the microwave resonator (reactor) for excitation of a bulk plasma. Preliminary experiments on deposition of diamond films using $H_2 + CH_4 + O_2 + Ar$ gas mixtures are reported. The deposition rate of diamond films on Si and Mo substrates placed on the 3" resistive heater in the microwave resonator depends on the position of the substrate and absorption of the microwave power in the plasma. At the power of 500 W the film growth rates of the order of 0.1 μm/hour were obtained in the central part of a circular area with diameter of 5 cm. Raman spectra of diamond films show main peak of D-band between 1331 and 1339 cm^{-1}. The diamond films are formed when the ratio of emission intensity from excited CH radicals to H_γ emission intensity is below $CH/H_\gamma = 4$.

1. Introduction

The microwave energy is very often used in devices for plasma assisted chemical vapor deposition (MPCVD) of diamond films, see e.g. [1]. Two most common types of the microwave plasma generation used in microwave plasma devices are: (i) an isotropic generation, and (ii) an anisotropic generation in a magnetic field, e.g. ECR. In both cases the yield of the microwave energy absorbed into the plasma and the resulting plasma parameters depend strongly on the microwave circuit which supplies the microwave power into the plasma. An isotropic generation is based on absorption of the microwave energy by the plasma without any preferential directions defined by external fields.

Typical devices for deposition of diamond films in an isotropic hydrogen-hydrocarbon plasma are either based on a downstream arrangement with tubular reactors passed through a rectangular waveguide with self heated Si substrates (by chemical reaction) or arranged as a microwave resonator containing bell jar vacuum chamber with an independently heated substrate. Upscaled microwave reactors with high power microwave generators are developed for large area MPCVD of diamond films using arrangements with ECR magnetic fields [2]. Most MPCVD devices are designed for deposition of films onto planar substrates. There are however problems remaining in deposition of films into holes, caves, or low diameter (< 10 mm) tubes.

In this work we present preliminary results obtained by novel microwave apparatus for plasma processing [3]. The device named the "SURFAJET" was developed to enable the plasma processing also on substrates with complicated surface geometry. The motivation for this work was to verify ability of the system for the deposition of carbonaceous and particularly diamond films.

2. Experimental microwave device SURFAJET

The SURFAJET microwave device is shown on schematic diagram in Fig. 1. The most important part of the device is a plasma slab generated in a quartz tube forming an plasma antenna immersed into a resonator cavity. The cylindrical cavity of 150 mm in diameter is coaxial with the plasma antenna (3 - 7 mm in diameter) and it serves at the same time as the reactor chamber. The adjustable shorting plunger installed on the bottom flange serves as both a tuning element and an ohmically heated (up to 800 °C) substrate holder. The plasma slab is generated by surfaguide launcher powered through the rectangular waveguide from 2.45 GHz magnetron of max 2 kW output power. The surfaguide launcher provides very effective heating of the plasma with reflected power typically much less than 10% [4]. For optimal resonance conditions in the system the waveguide is terminated by a shorting plunger. The impedance of surfaguide launcher can be matched by an adjusting plunger.

The interaction of hot parts of the quartz reactor tube with the hydrogen plasma in diamond MPCVD can often lead to a reduction of oxygen from SiO_2 which results in a Si coating. The Si coating absorbs the microwave power and causes further increasing of the wall temperature thereby enhancing the reduction process. Thus the process can finish by local melting of the tube and the vacuum leakage, particularly at higher microwave power. To avoid such problems the plasma antenna in the SURFAJET is arranged coaxially with the outer quartz tube serving as main vacuum wall. The most heated parts are cooled by forced air. The gas system feeds H_2 + CH_4 mixture (and eventual O_2 admixture) into the antenna tube while Ar is involved in between antenna and the outer tube. In this arrangement argon acts as a shielding gas. Moreover the antenna tube is arranged with an adjustable length using vacuum feedthrough. This enables either to optimize the antenna effect in resonant regimes or to work in downstream regimes where the antenna acts as a microwave plasma jet for the local film depositions, e.g. inside small size holes (diameter < 10 mm).

The heated substrate holder (3" in diameter) is electrically grounded. Potential of the plasma slab with respect to the ground can be affected by an auxiliary electrode

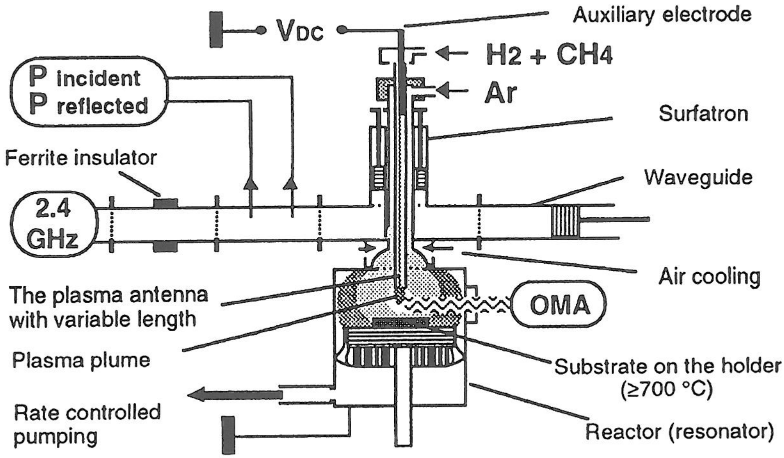

Fig. 1 The schematic outline of the experimental SURFAJET system.

immersed into the antenna tube, see Fig. 1. The electrode also acts as a conductive core of the antenna. This allows both to control flow of charged particles onto the substrate and at the same time to increase an absorption of the microwave power in the plasma.

3. Experimental procedure

Different compositions of $H_2 + CH_4 + O_2 + Ar$ gas mixture were examined for the growth of films. The films were deposited either on Si or on Mo substrates prescratched ultrasonically for 30 min in the submicron diamond powder emulsion in methanol. Typical experimental parameters used for the film deposition are as follows:

Duration of the deposition	60 - 900 min
Incident microwave power Pi	300 - 700 W
Total reflection Pr/Pi	≤ 10 %
Table temperature	≈ 800 °C
Summary gas flow	300 - 600 sccm
Gas composition (related to 100 % H_2)	0.5-2% CH_4, (< 0.5% O_2), ≤50% Ar
Total gas pressure in the vicinity of the substrate	2 - 10 Torr.

The gas pressure was controlled by the pumping speed. Optical emission spectra were detected by Optical Multichannel Analyser (OMA III). The resonant position of the tuning piston in the reactor was controlled by both a minimum of reflected microwave power and a maximum saturated ion current on auxiliary negative electrode (if used). The deposited films were examined by SEM and by Raman spectroscopy.

4. Results and discussion

Diamond films grown at circular areas 5 cm in diameter exhibit radial thickness inhomogeneity ≥ 10% with the maximum in the central part. The maximum film growth rate at microwave power P_i = 700 W is 0.5 μm/h. Inhomogeneity of the film thickness is given by low quality of the used resonator - stainless steel reactor, in which the plasma antenna is not able to generate dense bulk plasma and it acts predominantly as a downstream jet. The measurements of the reflected power P_r with respect to the position L of the shorting plunger in the reactor show low differences between the resonant and nonresonant positions, which reflect low quality factor of the resonator. Results for two different lengths l of the plasma antenna in the resonator are in Fig.2. It is seen that long plasma antenna can generate higher (short wavelength) modes.

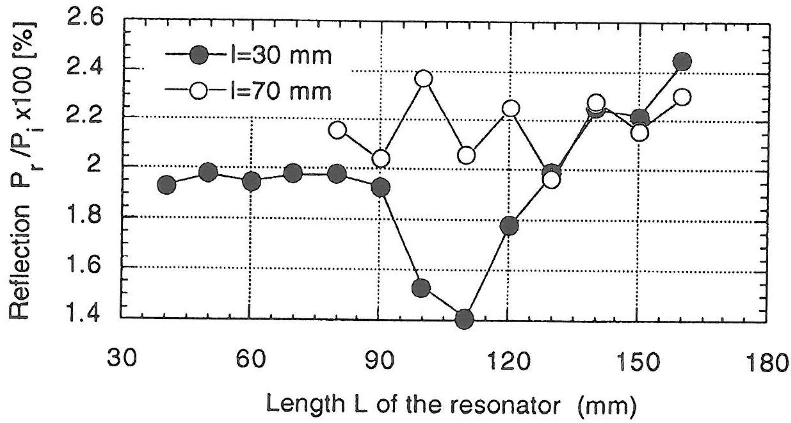

Fig. 2 The power reflection in the SURFAJET reactor vs. position of the shorting plunger at two different lengths l of the plasma antenna. P_i = 400 W, $H_2/CH_4/Ar/O_2$ = 300/3/100/1, p = 5 Torr.

The Raman spectra of films grown at 0.5% CH_4 in H_2 on Si in the the plasma "resonance" regime and the plasma jet regime are shown in Fig. 3. Growth of good crystalline quality films takes place mostly in the resonance regime and is characterized by nucleation kinetics. Films produced in the SURFAJET reactor are typically based on submicron diamond grains. The D-band peak in Raman spectra is usually located in the interval between 1331 cm^{-1} and 1339 cm^{-1}. At the methane contents close to 1% the graphite sp^2 content in films grows rapidly. Similarly in the downstream jet regime the films usually contain more graphite. We attribute this property to relatively low temperature of the substrate holder combined with a cooling effect of the flowing gas.

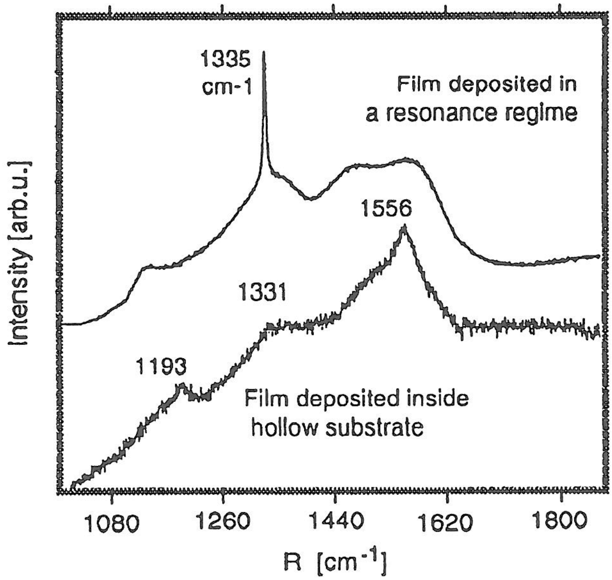

Fig. 3 Typical Raman spectra of diamond films deposited in SURFAJET reactor.

The plasma antenna in the SURFAJET allows utilization of additional DC (or RF) potentials. To illustrate this ability the electric current between the auxiliary electrode (cathode) and the grounded substrate holder through the plasma slab was measured as a function of an applied external DC voltage at different length of the antenna in the reactor. Fig. 4 shows, that the increasing voltage causes not only expectable growth of DC current, but also decrease of the reflected power. This means that the conductivity of the plasma grows up thereby enhancing the coupling between the plasma antenna and the plasma in the reactor. The plasma antenna with an extra electrode can become of technological importance not only for controlling of the particle flux, but also for an intentional doping of electrode metal into the growing films.

Observations of optical emission from the active plasma at the outlet of the plasma antenna confirm our previous experience with RF plasma jets [5]. To grow diamond films with minimum sp^2 graphite bonds it is necessary to find regimes where the ratio of optical emission intensity from CH radical (4300 Å system, (0-0) band) to that from hydrogen atoms H_γ (λ = 4340,5 Å) attains values $CH/H_\gamma \leq 4$.

The downstream arrangement has also been examined for depositions of films inside cylindrical holes 15 mm and 6 mm in diameter and 20 mm in depth with Mo rolled foil as a substrate. The plasma antenna was inserted into the hole to 1/3 depth. The experiment confirms possibility to grow films inside holes at about one order lower deposition rate than that at the planar surface. Different gas dynamics inside the hole requires an additional optimization of the process parameters. Deposition of diamond films by the surfatron plasma has been reported also by other authors [6].

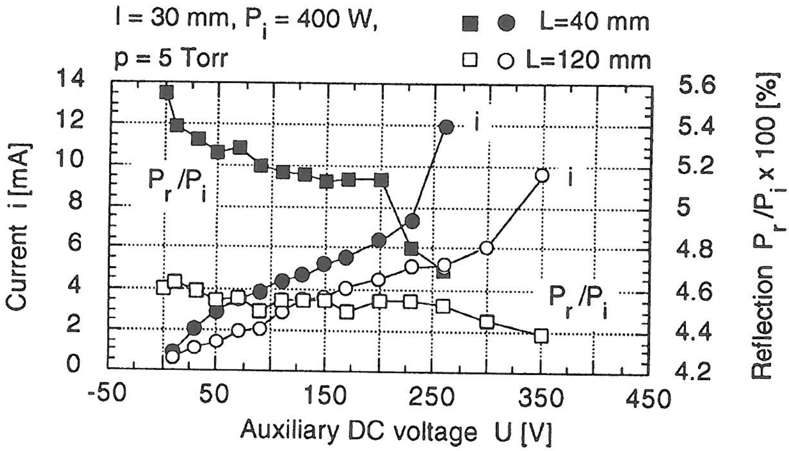

Fig. 4 Decrease of the reflected microwave power in the SURFAJET reactor as a function of the DC voltage in the plasma antenna slab at two resonator lengths L.

5. Conclusions

The novel microwave device for deposition of diamond films at rates up to 0.5 µm/h was successfully examined. Due to the arrangement with plasma antenna the device offers possibility to deposit films onto substrates of complicated geometry and simple utilization of an extra electrode for application of electric fields and better process control.

Supports by Swedish Natural Science Research Council (NFR) and the Swedish National Board for Industrial & Technical Development (NUTEK) are acknowledged.

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