A surface-wave driven plasma reactor for thin diamond film deposition: parametric study of the process parameter influence on film roughness

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Abstract

The influence of various process parameters on the film grain size and average roughness is investigated in a newly developed microwave plasma reactor. This reactor is based on a surface-wave-sustained discharge that yields a hemispheric plasma. This plasma hemisphere is used in a similar fashion as the plasma ball in the common bell jar and resonant cavity systems. Its advantages over these well known schemes are: no residual microwave power heating of the substrate, perfectly reproducible and high precision positioning of the substrate with respect to the hemispheric plasma tip, ease in achieving high microwave power density in the plasma and scaling-up capability. It is shown that grain size and roughness decrease with decreasing total gas pressure, with increasing substrate temperature, with increasing distance of the substrate with respect to plasma and with increasing microwave power density (above a threshold value). Addition of small amount of O_2 increases grain size and roughness.

Introduction

Thin diamond films can be achieved through chemical vapor deposition (CVD) with microwave discharges. We have shown recently that such discharges sustained by electromagnetic surface waves can be used to obtain high quality, uniform diamond films provided the reactor structure is designed in such a way as to yield a hemispheric plasma in front of the susceptor [1]. This reactor can then be employed to deposit diamond films in a similar fashion as with the plasma ball of the well known bell jar and resonant cavity systems. Such a surface wave reactor presents several advantages over these commonly used plasma ball systems: i) the substrate holder for diamond film deposition can be adjusted freely and reproducibly with respect to the distance from the plasma tip, enabling one to optimize the deposited film properties; ii) the substrate is not heated by residual microwave power: it can thus be kept at lower temperatures T_s, which is appropriate for delicate surface coating without the need of cooling it (typically, at 100 W/cm^3, T_s due to the plasma alone remains below 600 °C); furthermore, since it is uniformly heated, the deposit is more uniform; iii) higher power density can be absorbed efficiently in our plasma than in conventional resonant cavity and bell jar systems where power density does not usually exceed 40 W/cm^3 while we have achieved power density in excess of 140 W/cm^3; iv) the diameter of the plasma hemisphere can eventually be made larger than that of the plasma ball in conventional systems. These features were disclosed in our first paper on this new reactor [1]; in that same paper, we indicated briefly that the roughness of the film decreases with the power density absorbed in the plasma. The present communication is dedicated to examining the dependence of the deposited film roughness upon the process parameters; it follows a second paper [2] which considered the influence of the process parameters upon hydrogen atom concentration and gas temperature, and upon film properties except roughness.

The interest in low roughness film is related to the possibility of producing reliable membranes for X-ray lithography; in this application, the roughness of the diamond film must be the lowest possible to avoid diffraction. Another potential field has to do with low friction surfaces in micromechanics. We show below how to obtain low roughness and high quality diamond films by acting on the process parameters.

Experimental procedure

Figure 1 shows schematically the reactor used, which includes a plasma source sustained by microwaves at 2450 MHz, an independently heated susceptor and a dielectric cooling arrangement [1]. The substrate position d_{st} is defined with respect to the plane at which the the tube diameter changes abruptly. Monocrystalline silicon wafers with (100) orientation have been used as substrates. Samples of 2 cm diameter were submitted, prior to deposition, for 60 minutes to ultrasonic impacts of 20-40 μm diamond powder immersed in methanol. The substrate temperature T_s is controlled by an externally heated molybdenum susceptor and its value adjusted, thanks to an optical pyrometer, up to 1000° C. The gases used were premixed before entering the plasma, and the sum of H_2 and CH_4 flow rates was kept constant at 100 sccm. In the experiments below, the initial conditions (ultrasonic bath pretreatment and initial substrate conditions) are kept constant and we vary the total gas pressure p, the O_2 content, T_s, d_{st}, and microwave power P_{mw}.

As a rule, the deposition time was 3 hours. The morphology of the samples was examined with a scanning electron microscope (SEM); their diamond content was evaluated by macro-Raman spectroscopy in a backscattering configuration using an argon ion laser at 488 nm. Atomic force microscope (AFM) pictures were taken with a Nanoscope IIIA from Digital Intruments; the surface morphology of these films were visualized in a constant force mode ($f = 10^{-8}$ N) with microfabricated monocrystalline Si tips. The AFM pictures obtained were representative of a number of images taken for each sample with different tips.

Results and discussion

Roughness is low when both the size and size variations of the crystallites are small. To characterize the size variations, we use the parameter R_a that sums up (through an integral expression) the amplitude variations of the crystallites per unit surface area. Before presenting the results, we briefly summarize schematically the various mechanisms that determine the film roughness. Roughness depends very strongly on the initial nucleation density which is set in part by the substrate pretreatment (kept the same throughout the present series of experiments) and by the operating conditions. The higher the nucleation density, the more sites there are at which diamond crystals start growing; the more there are crystals growing, the sooner their individual growth stops, which occurs when the crystallites come into contact one with the other: they can no longer grow with their initial symmetry. In other words, the higher the nucleation density, the smaller the crystallite size. Further crystal growth goes on then through the renucleation (secondary nucleation) process, the new crystallites attaching through a non sp^3 bond to a point of the previous layer crystallites; this mechanism of secondary nucleation reproduces the initial pattern, giving birth again to small crystallites. In what follows, we examine the influence of the various operating parameters on the size of the crystallites, hence to some extent on the density of nucleation. The discussion that accompanies the presentation of these results is merely tentative.

Influence of the total gas pressure.- Table I shows that the crystallite size and R_a grow when increasing pressure p. Our explanation for the influence of p is based on the fact that the H-atom concentration increases with pressure, increasing the etching action of atomic hydrogen which tends to inhibit secondary nucleation (which implies a non-diamond phase bond with previously grown crystallites), thus favoring a larger growth of individual crystals. The H-atom concentration increases with p for two reasons: i) the electron temperature (or average electron energy) decreases with increasing p: hence, for a given microwave power density in the plasma, the electron density n_e increases with p (the power required to maintain an electron in the discharge decreases with the electron average energy); this leads to a higher dissociation rate of hydrogen molecules through electron collisions [3]; ii) thermal dissociation of the hydrogen molecule also increases with p since the gas temperature increases with p [1].

Influence of the substrate temperature T_s.- Table II shows that the crystallite size and R_a decrease steadily with increasing T_s. Two mechanisms seem to combine to explain these observations: i) nucleation density increases with T_s [4]; ii) as T_s increases approaching 1000° C, the etch rate of diamond by atomic hydrogen increases while that of graphite decreases [5], thereby increasing the probability of non-diamond phase retention as a second phase component, enhancing secondary nucleation.

Influence of the distance of the substrate from the plasma.- Table III shows that the crystallite size and R_a decrease as d_{st} is increased. The closest position reported, $d_{st} = 1.2$ cm, corresponds to the substrate being partly immersed in the plasma while for higher values there is no contact with the plasma hemisphere. We attribute this behavior to the fact that the concentration of H-atom decreases (through recombination into H_2) as we move away from the plasma source, thus favoring the formation of non-diamond phase structures.

Influence of the microwave power density.- We first recall that the volume of the plasma does not increase significantly with increasing microwave power P_{mw}, hence increasing P_{mw} essentially means increasing linearly the microwave power density absorbed in the plasma. Table IV shows that the film grain size and roughness decrease with increasing power density at large enough P_{mw} values. We believe that the mechanism that prevails to yield smaller grain size is the acceleration of ions onto the substrate which increases nucleation density [4]. This acceleration occurs through the boundary layer of the plasma hemisphere which results from the large gradient of electric field intensity across the boundary owing to the fact that microwave power is fully absorbed within the plasma hemisphere, hence this strong E-field across its boundary; acceleration of charged particles in a gradient of E^2 is known as the ponderomotive force [6].

Influence of the addition of O_2.- Table V shows that the grain size and R_a increase when adding a small percentage of O_2 to the discharge. The addition of oxygen modifies the composition of the carbon compounds and increases the amount of etchants: the preferential etching of non-diamond phase carbons by a greater number of H atoms [1] and other radicals such as atomic oxygen and other OH radicals favors the deposition of diamond compared with that of sp^2 carbons, and reduces secondary nucleation.

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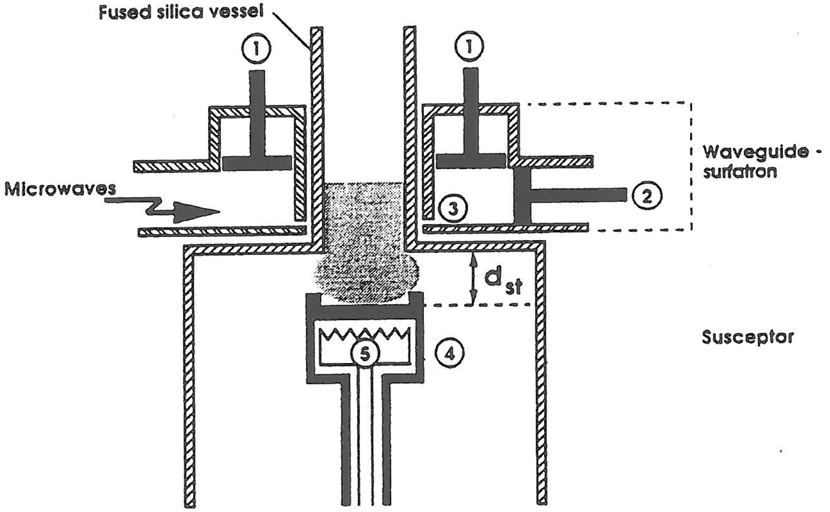

Figure 1. Schematic drawing of the reactor, including the plasma source and the independently heated susceptor (cooling arrangement not shown).

Table 1. Influence of the total gas pressure

p (torr)	R_a (nm)	Grain size (nm)
10	31	290
20	39	320
30	46	460
40	57	780

Table 2. Influence of the substrate temperature

T_s (°C)	R_a (nm)	Grain size (nm)
600	58	950
700	57	850
800	16	360
900	17	290
1000	13	230

Table 3. Influence of the distance of the substrate from the plasma

d_{st} (cm)	R_a (nm)	Grain size (nm)
1.2	31	360
1.6	25	320
1.9	24	310
2.3	20	285
2.5	19	260

Table 4. Influence of the microwave power

P_{mw} (W)	R_a (nm)	Grain size (nm)
600	20	250
800	17	240
1200	13	254
1500	10	200
1900	6	150

Table 5. Influence of the addition of O_2

%O_2	R_a (nm)	Grain size (nm)
0	31	260
0.15	35	280
0.30	56	460
0.50	72	910
0.75	74	950