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Low temperature and large area deposition of nanocrystalline diamond films with distributed antenna array microwave-plasma reactor

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ABSTRACT

Diamond films grown at low temperature (<400 °C) on large area of different substrates can open new applications based on the thermal, electrical and mechanical properties of diamond. In this paper, we present a new distributed antenna array PECVD system, with 16 microwave plasma sources arranged in a 2D matrix, which enables the growth of 4-inch nanocrystalline diamond films (NCD) at substrate temperature in the range of 300–500 °C. The effect of substrate temperature, gas pressure and CH_4 concentration in the total gas mixture of $H_2/CH_4/CO_2$ on the morphology and growth rate of the NCD films is reported. The total gas pressure is found to be a critical deposition parameter for which growth rates and crystalline quality both increasing with decreasing the pressure. Under optimized conditions, the process enables deposition of uniform (~10%) and high purity NCD films with very low surface roughness (5–10 nm), grain size of 10 to 20 nm at growth rates close to 40 nm/h. Nanotribology tests result in the friction coefficient of the NCD films close to that obtained for the standard tetrahedral amorphous carbon coatings (ta-C) indicating the suitability of this low-temperature diamond coating for mechanical applications such as bearing or micro-tools.

1. Introduction

Nanocrystalline diamond (NCD) films are outstanding material candidates that have attracted strong scientific and technological interests for optical, electronic, biomedical and tribological applications [1,2]. In fact, NCD films not only retain most of the extreme properties of microcrystalline diamond (MCD) but also exhibit a very low surface roughness due to their ultrafine (<20 nm) grains [3]. For instance, NCD coatings are highly desirable for the cutting tool industry [3,4] because smaller grain size enhances coating toughness and increases surface smoothness [3]. A smoother surface can facilitate chip evacuation, and thus significantly reduce cutting forces [4]. Recently, due to diamond's superior bulk thermal conductivity, NCD coatings on AlN or GaN [5,6] are being seriously considered as heat sinks on high-frequency and high-power devices where efficient heat removal becomes vital for maintaining the performance and reliability of these devices. However, low diamond adhesion to substrates and substrate damage during chemical vapor deposition (CVD) at high temperature are the limiting factors for its wider commercial use [7,8]. One of these limitations is in the typical CVD system conditions used for diamond growth such as hot filament or resonant-cavity microwave systems. As a matter of fact, these systems generally operate at temperatures as high as 800 °C in a harsh plasma environment. In addition, scaling up to larger deposition areas is particularly difficult and costly for microwave systems while hot-filament reactors suffer from contamination problems.

Therefore, there is an increasing demand for deposition systems that allow growing high purity NCD at lower temperatures and on larger areas. This demand leads to an increased interest and research effort in surface wave plasma systems for diamond synthesis that are more adapted to these requirements [9–12].

In this work, we present a new Distributed Antenna Array (DAA) CVD reactor for depositing NCD films at temperatures in the range of 300–500 °C by using $H_2/CH_4/CO_2$ gas chemistry. This reactor is based on 16 microwave coaxial plasma sources arranged in a 2D matrix. The reactor does not have physical limitations since the number of elementary sources can be increased allowing an easy up-scaling to grow large area diamond films. Moreover, lower pressures than in conventional diamond CVD processes have to be used allowing limiting plasma heating of the substrate, and thereby maintaining low substrate temperatures. However, much lower deposition rates are obtained.

In the DAA reactor, the influence of substrate temperature, total pressure and CH_4 concentration on the morphology, structure, uniformity, growth rate and friction coefficient of NCD films grown on Silicon was investigated using techniques such as scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), Raman spectroscopy, thin film reflectometry and rotational mode of a ball-on-disk nanotribometry.

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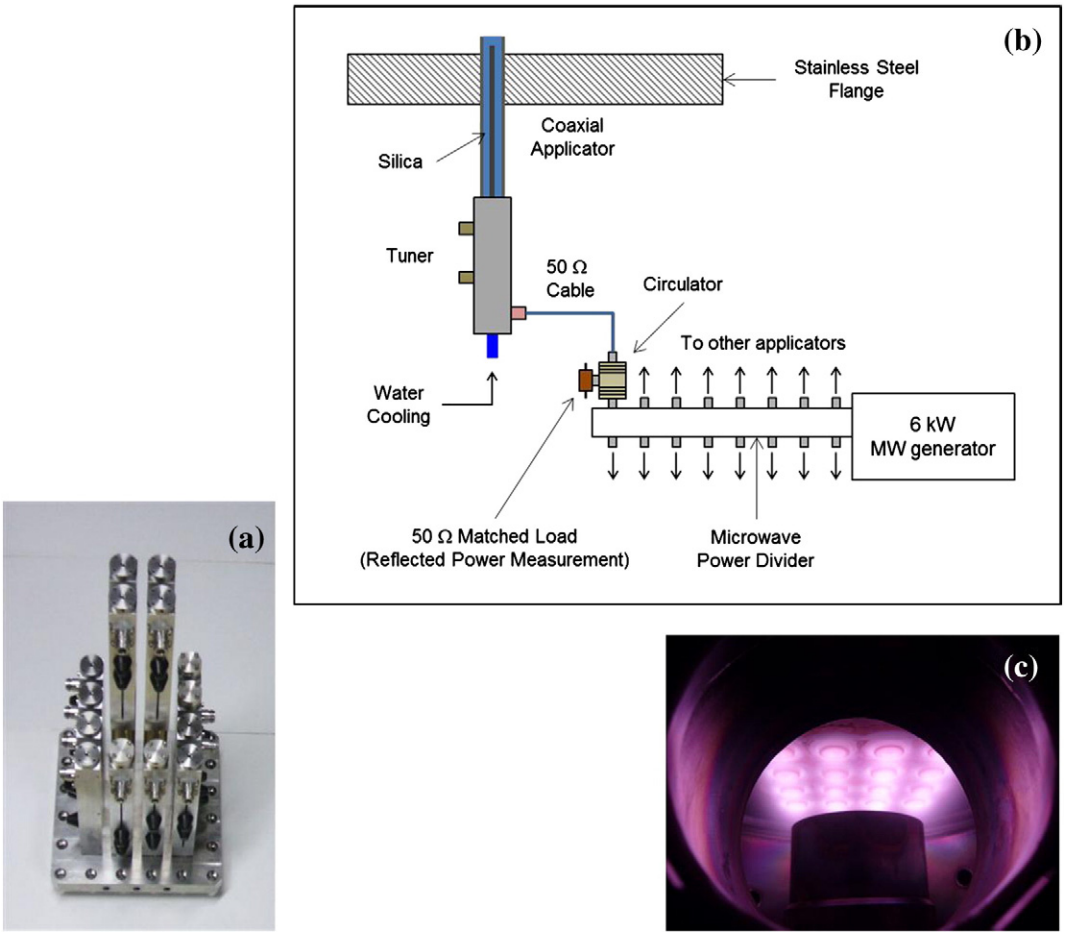

Fig. 1. (a) 16 coaxial plasma sources inserted in a square metallic flange arranged in a 2D-matrix to constitute the distributed antenna array (DAA), (b) Design of a coaxial plasma source, (c) View of the ignited plasma sources inside the chamber.

2. Experimental details

The DAA reactor consists of 16 coaxial plasma sources inserted in a square metallic flange and arranged in a 4×4 matrix (Fig. 1a) fed by a 6 kW microwave generator. Initially, this technology has been developed for ECR plasma [13] (i.e. the source extremity is equipped with a permanent magnet) but in our case, taking into account the working pressure close to 1 mbar, plasma sources are free from magnetic field. Microwave power is coupled to the system using antennas appropriately introduced into a rectangular waveguide. The microwave energy is then transported to the sources inside the chamber, thanks to coaxial cables (Fig. 1b). This arrangement leads to dividing power between the 16 sources (i.e. around 180 W/source). Discharge is then ignited around each source inside the chamber of the low-pressure reactor (Fig. 1c), and the plasma diffuses to the substrate. When the microwave power is increased, the localized plasmas expand and then meet together to produce a sheet of uniform plasma. Taking into account the distance between each elementary source, the substrate holder must be localized at least at 40 mm from the plane sources. Due to this configuration, even conductive substrates with sharp edges can be uniformly coated without disturbing the electric field. However, due to the low pressure operating regime, low plasma density and low molecular hydrogen concentration as compared to conventional high-power high-pressure CVD reactor are obtained. In order to compensate for the low etching of non-diamond phases due to the lack of atomic hydrogen, CO_2 is added to the gas mixture, as reported by other studies [9–12]. It is important to note here that reactors working at low pressure and low temperature have already been presented in the literature [9,11] but these studies are mainly based on surface wave plasma reactor which are well known to have a plasma density limited by the critical plasma density (7.5×10^{10} electrons·cm^{-3} at 2.45 GHz). Moreover, in such a kind of reactor, microwave applicators present large silica surfaces which, due to the use of hydrogen plasma, can be etched and lead to film contamination. In the case of DAA reactor, thanks to the small size and optimized design of each elementary source (coaxial applicator), the ignited plasma has been demonstrated to reach density up to 10^{12} electrons·cm^{-3} [14] which will lead, for similar microwave power, to a more efficient chemical species production. The reduced size of sources also allows limiting silica surfaces in the reactor and then contamination of grown layers. The last point that can be highlighted here is that there is no limitation to upscale the reactor by increasing the number of sources and a 3D distribution of the sources can be imagined in order to allow diamond deposition on complex shapes.

Prior to seeding, polished 2 inch Si wafers with thickness of around 250 μm (p-type, 1–3 Ω·cm, semiconductor grade) are ultrasonically cleaned in acetone, then etched by HF acid (20 vol.%) to remove the

Table 1
Sample ID and the corresponding growth conditions.

Samples[a]	A	B	C	D	E	F
Pressure (mbar)	0.5	0.35	0.5	0.5	0.5	0.5
Substrate temperature (°C)	400	400	400	400	300	500
[CH_4] (%)	2.5	2.5	1	5	2.5	2.5
[H_2] (%)	96.5	96.5	98	94	96.5	96.5
Film thickness (nm)	207	189	218	200	196	202
Deposition time (min)	417	281	477	360	440	332

[a] All samples were grown at a microwave power of 3 kW, 1% of CO_2 and total gas flow of 50 sccm.