DIAMOND FILM DEPOSITION IN AN INDUCTIVELY COUPLED PLASMA REACTOR

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Abstract

An inductively coupled (RF) plasma (ICP) system was developed and operated for diamond film deposition. A thermodynamic analysis, a kinetic analysis for the chemical dissociation and a mathematical model for flow and temperature fields have been developed in an attempt to describe plasma enhanced chemical vapor deposition (CVD) processes for diamond film in the C-H-O and C-H systems. The analysis results shows that the substrate temperature may be lowered by presence of oxygen in the feed gases and the thickness of the boundary layer is a key for diamond deposition. Diamond films have been successfully deposited from three gas mixtures: CH_4-H_2, C_2H_2-H_2, and C_2H_2-H_2-O_2. The diamond-like carbon and amorphous carbon films may also be generated in this system. Diamond films can be formed at a lower substrate temperature, below 800 ^{o}C, by adding oxygen into the mixture. The film growth rate was about 10-15 μm/hr over a 20 mm diameter area of the substrate and the crystal size ranged from 1 to 2 microns. The films were characterized by laser Raman spectroscopy, scanning electron microscopy, x-ray diffraction, and x-ray photoelectron spectroscopy.
KEYWORDS: diamond deposition, plasma, thermodynamics, kinetics

Introduction

Diamond has many superb properties, such as: hardness, thermal conductivity, electrical insulation, optical transparency, and chemical stability. These properties have allowed the development of many applications related to mechanical, electronic, optical, and military uses. Theoretically, diamond can be produced by an equilibrium phase transformation from a solid stable phase of graphite to a metastable phase of diamond at high pressure and high temperature (HPHT process). This process was commercialized in the 1950s [1,2].

Chemical vapor deposition (CVD) is a process that the vapor species chemically react to form a continuous film on a substrate. Thermal plasmas are favorable choices as a heating source for processing. Table 1 outlines some diamond deposition methods. Each method has its own characteristics and potential for commercialization. For example, an ICP system for the deposition produces diamond films with high quality, since there are no electrodes in the heating source. It also

Table 1. Comparison of diamond deposition methods

Method	ICP	DC	Microwave	Filament	Flame
Power kw	1 ~ 100	1 ~ 100	~ 1	< 1	-
MW#	< 1	< 10	-	-	-
CH_4/H_2, %	< 5	0.1 ~ 5	< 3	< 2	-
Sub. temp., °C	700 ~ 1,000	800 ~ 1,200	600 ~ 1,100	800 ~ 1,100	500 ~ 1,000
Linear growth rate, μm/hr	10 ~ 200	< 1,000	< 40	1 ~ 20	< 800
Gas temp., °C	> 4,000	> 4,000	> 4,000	< 2,000	< 3,000
Pressure, Torr	10 ~ 760	25 ~ 760	< 50	1 ~ 760	~ 760
Deposit area	large	small	large	medium	small

power related to the commercial scale in use.

offers a large column hot stream with a potential for a high volumetric growth rate. Matsumoto et al [3] first demonstrated the possibility of diamond CVD in an atmospheric pressure ICP system [4~6]. It was stated that the volumetric growth rate in an ICP system would be 4~5 times higher than in a DC plasma system although the latter has a higher linear growth rate. In addition, if a system can use some oxygen in the feed gases, the deposition may be operated at a low substrate temperature, allowing more choices for the substrate materials. Compared with the other methods, the ICP system might be one of the best choices for this purpose. The previous studies from microwave plasma system [7~9] show that oxygen species may accelerate the preferential etching of the non-diamond phases. Harris and Weiner [10] pointed out that O_2 addition allowed diamond films to be grown under composition and temperature conditions which otherwise would produce largely non-diamond carbon. Mucha et al [11] also demonstrated that oxygen additions to CH_4/H_2 discharges increased the concentration of atomic hydrogen, raised the number of active diamond growth sites, and enhanced the growth rates. Hence, oxygen has the potential for both improving the deposit quality and extending the temperature range for diamond formation. Our research utilizes some oxygen in an ICP system to demonstrate the feasibility of diamond deposition in a C-H-O system, especially at lower substrate temperatures.

Thermodynamics

To understand the formation of chemical species and potential of diamond

deposition at a low substrate temperature, a thermodynamic analysis method is proposed for the C-H-O system. The detail is described in the reference [12]. Three conclusions can be drawn from the analysis. Firstly, there is a critical C/H ratio for the choice of hydrocarbon gas in the mixture. Without oxygen present, diamond deposition requires a highly diluted hydrocarbon mixture (by hydrogen). Secondly, the O/H ratio is a very important parameter for deposition from the C-H-O mixture. Above a critical value, O/H ≈ 0.75, the system is in a non-growth region. Below this value each input gas must meet a criterion indicated by the line. Thirdly, the system can be operated at a low substrate temperature for diamond deposition. This analysis led to the experiments with an appropriate choice for the input gases.

Mathematical Model for Flow and Temperature Fields

By the evidence from the thermodynamic analysis, the primary experiments were designed and performed. All were not successful even though the appropriate ratios of carbon, hydrogen and oxygen were maintained. The failure of the preliminary experiments led to the need for an understanding of the flow and temperature fields in the reactor.

For a two-dimensional problem in a cylindrical coordinates (r, θ, z), a general formulation for the equations can be written as,

$$a_\varphi\left[\frac{\partial}{\partial z}\left(\varphi\frac{\partial\psi}{\partial r}\right)-\frac{\partial}{\partial r}\left(\varphi\frac{\partial\psi}{\partial z}\right)\right]-\frac{\partial}{\partial z}\left[b_\varphi r\frac{\partial(c_\varphi\varphi)}{\partial z}\right]-\frac{\partial}{\partial r}\left[b_\varphi r\frac{\partial(c_\varphi\varphi)}{\partial r}\right]+r d_\varphi=0$$

The coefficients and variables ω, stream function ψ, and enthalpy h, are listed in

Table 2 The general elliptic equation

#	φ	a_φ	b_φ	c_φ	d_φ
1.1	ψ	0	$\frac{1}{\rho r^2}$	1	$-\frac{\omega}{r}$
1.2	$\frac{\omega}{r}$	r^2	r^2	m	$-r\left[\frac{\partial}{\partial z}\left(\frac{u^2+v^2}{2}\right)\frac{\partial\rho}{\partial r}-\frac{\partial}{\partial r}\left(\frac{u^2+v^2}{2}\right)\frac{\partial\rho}{\partial z}\right]$
1.3	h	1	Γ_h	1	$-\frac{1}{r}\frac{\partial}{\partial z}\left[\mu\cdot r\left(1-\frac{\partial(v^2/2)}{\partial z}\right)\right]-\frac{1}{r}\frac{\partial}{\partial r}\left[\mu\cdot r\left(1-\frac{\partial(v^2/2)}{\partial r}\right)\right]$

Typical result from the model are given in [12].

Experimental Results

A schematic for the ICP diamond CVD process is shown in Fig. 1. The main part of the system is the deposition reactor which includes a 50 kW TAFA model 66 RF plasma torch, a vacuum quench chamber, and a movable substrate holder. The experiments were operated at different plate power settings that ranged from 18 to 21 kW and the radio frequency 3.2 MHz. The power coupled to plasma gas was 5~8 kW as calculated by the heat balance. A 20 × 20 × 0.5 mm^3 molybdenum or (100) oriented silicon substrate was bolted on a ϕ40 mm steel plate on which the substrate was 55~105 mm below the end copper coil in the torch. The copper substrate holder was designed with a water spray unit for a uniform temperature on the surface. The

substrates were first mirror-polished with 3~6 mm diamond paste for about 10 min. and ultrasonically cleaned in an acetone/methanol bath for 30 min. A thin paper cup was used to cover the substrate to protect the surface from contaminants before the experiment. Based on the thermodynamic analyses, three types of the feed gas mixtures, Ar-CH_4-H_2, Ar-C_2H_2-H_2, and Ar-C_2H_2-H_2-O_2, were chosen for the preliminary experiments. The percentage of C/H in the above three mixtures was correspondingly chosen to be 0.75, 0.4, and 0.8~1.05 (O/H = 0.25~0.4%). The substrate surface temperature was measured and the calorimetric energy balance performed. The deposition reactor was first evacuated to less than 0.1 atm and flushed with argon for over 5 minutes. The ICP torch was ignited in a pure argon and the system pressure was controlled at 0.4 atm during the experiments.

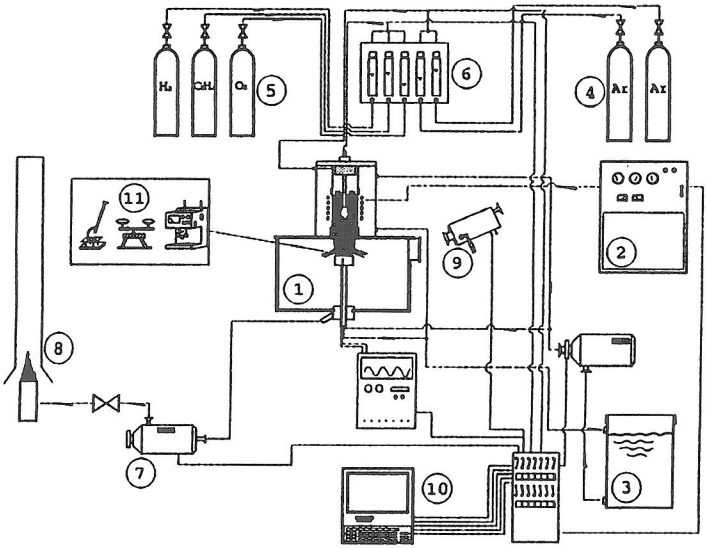

Fig. 1 Schematic of the Experimental System.
1. ICP/CVD Reactor 2. Power Supply 3. Cooling System 4. Plasma Gas 5. Reactive Gases 6. Flowmeters 7. Vac. Pump 8. Burner 9. Two color Pyrometer 10. Data Acquisition System. 11. Sample Analysis.

Experimental Result

The experimental results reported here are from the molybdenum substrate material. All of the deposits from CH_4-H_2, C_2H_2-H_2, and C_2H_2-H_2-O_2 were a gray/dark gray in color and uniformly covered a ϕ20 mm area on the substrate. The film growth rates were about 10 micron/hr and the crystal size is about 1~2 micron in all cases. The substrate temperatures were about 850~950 ^{o}C. The films were characterized by laser Raman spectroscopy, scanning electron microscopy, x-ray diffraction and x-ray photoelectron spectroscopy without any additional treatment.

1. Laser Raman Spectroscopy

Laser Raman spectroscopy is used to detect the polymorphies of carbon. Typical result [12] show that the film has one sharp peak at 1333 cm^{-1}. It is well known as

the CVD diamond peak. In addition, a weak peak at about 1580 cm^{-1} indicates the presence of graphite-like phase.

2. Scanning Electron Microscopy and X-Ray Diffraction

The SEM micrographs of deposits from two mixtures are shown in Fig. 2 (a)~(b). It can be seen that the diamond crystals at the growth surface are well-faceted, dense, and uniform. In the CH_4-H_2 mixture, the crystal facets are preferentially oriented with the cubo-octahedral face planes or the combination of (100) and (111) facets, which agrees with the x-ray diffraction results. In the C_2H_2-H_2 mixture, the crystals are oriented with octahedral face planes or (111) facets and in the C_2H_2-H_2-O_2

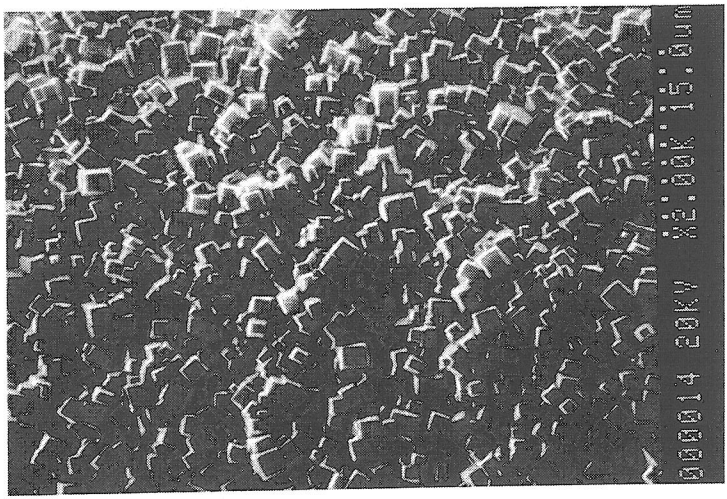

Fig.2 (a) C_2H_2-H_2-O_2 Mixture, C/H=1.2%, O/H=0.4%

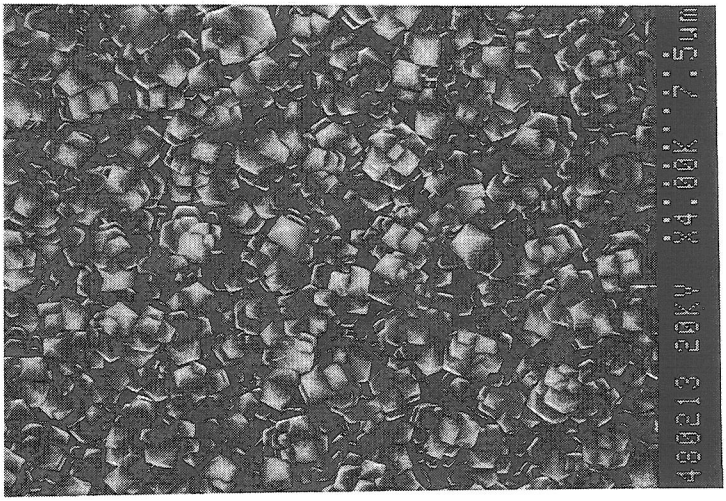

Fig. 2(b) C_2H_2-H_2-O_2 at Low Substrate Temperature, C/H =0.8%, O/H=0.3%

mixture with cubic face planes or (100) facets. This observation conforms to the orientation rule of diamond crystals based on a relation between C/H ratio and growth habit plane.

Conclusions

Diamond films have been deposited from three feed gas mixtures: CH_4-H_2, C_2H_2-H_2, and C_2H_2-H_2-O_2 in an ICP system. The growth rate is about 10 micron/hr on molybdenum substrate and the discrete crystal size ranges from 1 to 2 micron. The substrate temperature is below 900 ^{o}C. The thermodynamic analyses for diamond deposition in C-H-O system showed that the substrate temperature could be lowered by oxygen species at a moderate pressure compared with atmosphere; A higher temperature source is needed for a high growth rate; A system operated at a medium level of pressure might enhance the growth rate; O/H ratio is a very important parameter for the deposition; Hydrocarbon gas can be increased over 1.0 of C/H ratio only with oxygen present and the C/H ratio should be very low without oxygen in the input gases; C_2H_2 might be a very favorable hydrocarbon gas for diamond deposition in the C-H-O system.

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