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Optical emission spectroscopy study of positive direct current bias enhanced diamond nucleation

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Abstract

High nucleation density and crystalline diamond films were deposited on a mirror-polished Si(100) substrate by horizontal microwave plasma chemical vapor deposition using a two step process consisting of positive direct current (dc) bias enhanced nucleation and growth. Optical emission spectroscopy was employed to investigate *in situ* the plasma emission characterization during positive biasing process. Emission lines from the Balmer series of atomic hydrogen, molecular hydrogen, CH, C_2, and Ar were observed in the visible and ultraviolet ranges when CH_4, H_2, and Ar were used as the reactant gases. The dependence of plasma emission spectra on the deposition parameters, such as biasing voltage, methane concentration and working pressure was investigated. The relative concentrations of neutral atomic hydrogen were estimated by using the Ar emission at 750.4 nm as an actinometer. A significant variation in the emission intensity of the radicals was measured with a change in the biasing voltage. The correlation between the spectra of some species and the quality of diamond films was studied. The results show that CH and C_2 both were important precursor in the diamond deposition, while C_2 was associated with the presence of amorphous phase in the films during positive dc biasing process.

Keywords: Direct current; Optical emission spectroscopy; Diamond; Microwave plasma chemical vapor deposition

1. Introduction

Bias enhanced nucleation (BEN) process was used by many researchers to grow heteroepitaxy diamond films on silicon substrate [1–4]. The conventional diamond-scratching method used to promote nucleation was eliminated, making it possible to nucleate diamond on pristine substrate. During BEN process, a negative direct current (dc) bias (−200 to −300 V) was usually used to enhance diamond nucleation at high methane concentration for a period of time. High nucleation density approximately $10^{10}/cm^2$ was achieved after BEN step and highly oriented diamond was observed after deposition. In negative BEN process, an amorphous carbon or SiC buffer layer or an increase in surface mobility plays an important role in the growth of diamond films. In positive BEN process, a closed layer epitaxially oriented cubic SiC with a thickness of about 10 nm is the diamond–silicon interface is often observed. A number of mechanisms [5–8] of bias enhanced nucleation have been proposed but the mechanisms leading to the nucleation are still not well understood. In order to elucidate the growth mechanism, numbers of *in situ* detection methods have been developed to diagnose the gas species presented in the plasma. One of the important methods for characterizing gas phase species is optical emission spectroscopy (OES) which is a non-invasive technique that enables to monitor individual optically emitting intensity of plasma species. The method has been popularly used in microwave plasma, dc plasma, and combustion flame in recent years [9–14]. In plasma chemistry created by biasing environment, it is important to investigate the changes of several radicals that contribute to the formation of diamond. Some researchers have shown the results in the plasma chemistry during negative dc BEN process. Stoner et al. [15] proposed that the nucleation density of diamond was increased when the strong plasma glow was formed near the substrate surface. Shigesato et al. [16] proposed a mechanism for the enhanced nucleation density that assumed increased concentrations of atomic hydrogen due to the bias voltage to be able to stabilize diamond nuclei on the substrate surface. Jackman et al.

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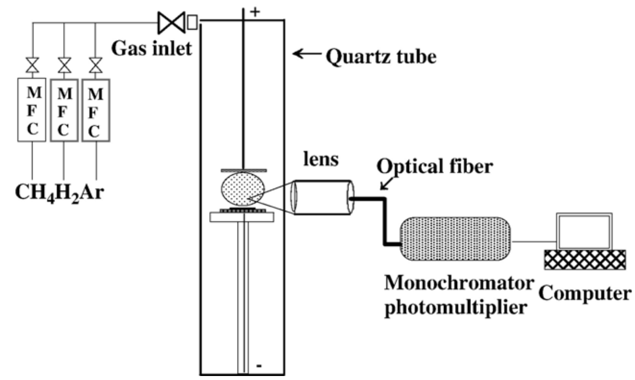

Fig. 1. Schematic diagram of illustration of experimental apparatus for diamond deposition and optical emission spectroscopy.

[17] performed the measurement at 2.66 kPa, indicating a pressure dependence of [H] under bias condition on tungsten substrate. Barshilia et al. [18] showed that the chemical species increased significantly for a negative dc bias $|V_b|>60$ V in microwave plasma enhanced chemical vapor deposition (MPCVD). The higher concentration of excited species and the associated effects played a significant role in the diamond growth process.

In previous study [19,20], we have reported diamond nucleation enhanced by a positive dc bias, in which high nucleation density and polycrystalline diamond were grown well on Si substrate. For a better understanding of positive BEN process in MPCVD, the optical emission spectroscopy was used to study the effect of positive dc bias during the nucleation of diamond. However there are some limitations in using OES because it only provides partial information on the plasma compositions. From OES spectra it is usually straightforward to identify the emitting species and follow qualitative changes in plasma properties as a function of external parameters such as gas composition, radio frequency or microwave power, etc. It is difficult to determine the absolute concentration of reactive species in the plasma by optical emission due to the complicated excitation and transition processes. In order to estimate the concentration of neutral atomic hydrogen the Ar line at 750.4 nm was used as an actinometer [21]. The intensity ratio of H_α (653.6 nm) to Ar (750.4 nm) was used to measure hydrogen atom concentration because of the similar excitation energies responsible for the two emission lines (H ~ 12.1 eV, Ar ~ 13.5 eV). Although the excitation thresholds for H_α and Ar lines differ by ~ 1.5 eV, they are strong and well isolated from other lines. The purpose of present study focused on qualitative statements of variation of atomic hydrogen, CH, C_2 and electron temperature with bias voltage in the plasma characteristics. The effects of methane concentration and working pressure on chemical species during positive dc biasing were also investigated.

2. Experimental details

The diamond films were grown in a standard tubular microwave plasma chemical vapor deposition apparatus. A gas mixture of methane–argon–hydrogen was used as the reaction source. A small amount of argon (1%–2%) was added to the methane–hydrogen gas mixture to act as a calibration tool for the OES studies. A positive dc bias was applied to the Si substrate between 0 and +300 V. In previous study, this arrangement has been used to grow good quality polycrystalline diamond on silicon substrate and biasing at +300 V with a significant enhancement in the nucleation density. The ion current was in the range of 0–50 mA, depending on the substrate bias voltage between 0 and +300 V. The activated species in the plasma during the deposition processes were analyzed by the OES technique in the 200–900 nm range. The system used for OES experiments was a SOFIE instrument DIGITWIN SEM/S/U20 system. The resolution was 0.5 nm and the available spectra range was 200–900 nm. The monochromator was connected to the plasma reactor via a bundle of optical fibers ensuring the electrical isolation and light transmission from the plasma to the entrance slit. The optical emissions focused by a quartz lens with a focusing length of 20 cm were transferred from the plasma center near the deposition surface to monochromator through the optical fibers. The optical device (optical fiber, monochromator, photomultiplier) response was calibrated with a calibration lamp in the front panel of the rack monochromator at known temperature, to provide absolute measurement of the atom density. A schematic diagram of illustration of experimental apparatus for diamond deposition and plasma emission spectroscopy is shown in Fig. 1.

Species in the plasma were activated by decomposition and recombination of methane and hydrogen. The lines H_α (656.3 nm), H_β (486 nm), C_2 (swan band at 516 nm), CH (431.3 nm), Ar (750.4 nm), were monitored at plasma center as a function of substrate bias condition, methane content, and gas pressure of the plasma feedstock gases. The emission lines of the species are listed in Table 1 [18]. Calibration of H_α signal was achieved by comparing with Ar signal at 750.4 nm. The ratio of H_β to H_α is commonly taken to reflect the behavior of mean electron temperature within the plasma. The two carbonaceous peaks, CH (431.4 nm) related to CH_x species in plasma were precursors of diamond, and C_2 (473.7 nm) related to C_2H_x species increasing the non-diamond content in deposited films in the spectrum was also measured.

3. Results and discussion

3.1. Microstructure of nucleation step

Fig. 2(a) shows a typical surface morphology of silicon substrate treated with positive bias +300 V for 5 min and other deposition conditions at 350 W, 4 kPa, $CH_4/H_2=35/100$ and 800 °C. The high methane concentration of 25.92% was used

Table 1
Optical emission lines observed in plasma for gas mixture of methane and hydrogen [18]

Species	Transition	Peak position (nm)
H_α	$n'=3\rightarrow n=2$	656.1
H_β	$n'=4\rightarrow n=2$	486.1
CH	$B^2\Delta\rightarrow X^2\Pi$	387.0
	$A^2\Delta\rightarrow X^2\Pi$	431.5
C_2	$d^3\Pi_g\rightarrow a^3\Pi_u$	516.3