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Investigation on the influence of high deposition pressure on the mcirostructure and hydrogen impurity incorporated in nanocrystalline diamond films

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ABSTRACT

The impact of high deposition pressure on the microstructure and incorporation hydrogen impurity within nanocrystalline diamond (NCD) films have been investigated in a home-made microwave plasma chemical vapor deposition (MPCVD) apparatus when the microwave power and the substrate temperature were kept constant at 800 W and 650 °C, respectively. It is found that high deposition pressure not only influences the grain size and quality, but has conception link with the form and content of the bonded-H incorporated in NCD films. With the deposition pressure increases from 10 kPa to 30 kPa, the average grain size decreases from 33 nm to 13 nm and a large amount of hydrogen is detected in the obtained NCD films by Fourier transform infrared spectroscopy (FTIR). Particularly, the NCD films deposited at 15 kPa possesses the largest amount of the bonded H impurity. The optical emission spectroscopy (OES) from the plasma indicates that the intensity ratio between H_α and C_2 decreases with the increase of the deposition pressure, which suggests the decline energy levels for the excited H atoms. Based on these experimental results the role of high deposition pressure on the growth of NCD films is discussed.

1. Introduction

Nanocrystalline diamond (NCD) films not only retain the excellent properties of polycrystalline diamond films, but also overcome their disadvantage of high surface roughness [1,2]. And the small grain size, ranging from several hundreds of nanometers to a few nanometers, makes NCD films receive great attentions and be considered as a promising candidate for these new applications, such as bio-medication, optoelectronic devices, laser window, field emission display and quantum information [3–5]. Recently, the color centers of nanocrystalline diamond have been successful applied to obtain single photon emission [6,7], which promotes further investigations on the impurity conditions in NCD films.

Nowadays, the dominating deposition technologies which have successful been applied in the industry and research facilities are hot filament chemical vapor deposition (HFCVD) and microwave plasma chemical vapor deposition (MPCVD) [8,9]. And it is also known that in comparison of HFCVD, MPCVD is an effective method to prepare high quality diamond films due to the electrodeless discharging plasma [10]. However whichever technique is being used, hydrogen in diamond films is always a common focus [11]. Commonly a few percentage of CH_4 diluted in hydrogen or argon is the primary feeding gas for the deposition of NCD films and H atoms play an important role on the growth of diamond films. In the case of the standard growth mechanism of CVD diamond, the effect of H atoms is not only related to the hydrogen concentration in source gas mixtures, but also have conception link with the main active species [12,13]. So far, the impurity of H atoms has been considered as a ubiquitous and important issue to NCD films, which can produce point defects and influence the electrical properties [14]. In general, the behavior of incorporating bonded hydrogen in NCD films mainly occurs in the growth process, and therefore it is significant to research the effect of growth conditions on the hydrogen impurity in NCD films.

As is known to all that CVD diamond is the overall thermodynamic effects of the growth parameters [15]. For the MPCVD technique, the structure and quality are dramatically influenced by the microwave power, pressure, substrate temperature as well as the gas mixtures. From the aspect of crystal growth, it is necessary to investigate and identify the role of each growth parameter, especially the role of the microwave power and the deposition pressure which are of much

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important parameters [16]. For the microwave power, some reports have pointed out that increasing microwave power is an effective way to improve the quality, uniformity and growth rate of NCD films [13]. Providing further introducing a small amount of nitrogen and oxygen, the growth rate of NCD films can be increased dramatically with the production of a high density of lattice defects, especially the H atoms induced point defects [17]. Besides that increasing deposition pressure is also an effective way to increase plasma density, particularly the deposition pressure is higher than 10 kPa [18]. And that deposition condition should have some effects on the growth of NCD films.

In this work, some experiments have been carried out in a home made MPCVD apparatus using Ar/CH_4/H_2 mixture as feeding gases in order to research the effect of high pressure on the morphology, quality and hydrogen impurity incorporated in NCD films. Although the total amount of hydrogen impurity in NCD films have been characterized by employing nuclear magnetic resonance (NMR), forward-recoil spectroscopy (FRES), second ion mass spectroscopy (SIMS) and elastic recoil detection analysis (ERDA), Fourier transform infrared spectroscopy (FTIR) is still a powerful and effective tool to analyse the conditions of hydrogen impurity, especially the bonded hydrogen with various incorporation forms in NCD films such as sp^3CH_x (x = 1, 2, 3) [14,19]. In our investigation, FTIR is used to investigate the content and form of bonded hydrogen defects in the NCD films. The results are useful to understand the mechanism of incorporating bonded hydrogen impurity into NCD films and shed light into exploring the high deposition pressure condition for NCD films growth.

2. Experimental details

All the diamond samples are deposited in a home-made 1.0 kW MPCVD system, of which the schematic is illustrated in Fig. 1(a). It is notable that an intermediate frequency (IF) heater device is set in the stage. The IF heating temperature is measured and controlled with a temperature controller which can keep the temperature variation smaller than 15 °C. In order to further reduce the effect of temperature variation on substrate, a quartz holder with the total height of about 14 mm is set on the IF heater device. In our experimental process, the substrate temperature of 650 °C with about 5 °C in variation, determined by a two-color optical pyrometer, were obtained when the temperature of the IF heater device was set at 550 °C. Besides that, both of the chamber and the coaxial antenna are cooled by the compressed air.

To confirm the discharging condition at high deposition pressure with the designed quartz holder, the computer simulations about Ar plasma at 30 kPa generated by 800 W are performed using the commercial software Comsol Multiphysics. For our plasma model, the electron density is computed by solving a pair of drift-diffusion equation:

$$\frac{\partial n_e}{\partial t} + \nabla\cdot\Gamma_e = R_e - (\mathbf{u}\cdot\nabla)n_e$$
$$\frac{\partial n_\varepsilon}{\partial t} + \nabla\cdot\Gamma_\varepsilon + \mathbf{E}\cdot\Gamma_e = S_{en} - (\mathbf{u}\cdot\nabla)n_\varepsilon + (Q + Q_{gen})/q \tag{1}$$

where n_e and $n_\varepsilon$are the electron density and the electron energy density, $\Gamma_e$and $\Gamma_\varepsilon$are the electron flux and the electron energy flux, R_e is the electron source, $\mathbf{u}$ is the neutral fluid velocity by the gas flow, S_{en} is the electron energy loss by inelastic collision, Q is plasma reaction heat source, Q_{gen} is the other heat source. The transports of neutrals (Ar) and ions (Ar^+) are simulated with Maxwell-Stefan equation:

$$\rho\frac{\partial \omega_k}{\partial t} + \rho(\mathbf{u}\cdot\nabla)\omega_k = \nabla\cdot\mathbf{j}_k + R_k \tag{2}$$

where $\rho$is the density of mixture gas, $\omega_k$is the mass fraction of the heavy species, $\mathbf{j}_k$ is the diffusive flux vector of the heavy species, R_k is the rate coefficient of the heavy species. The high frequency electric field in this MPCVD reactor is computed using the following equation:

$$\nabla \times \mu_r^{-1}(\nabla \times \mathbf{E}) - k_0^2(\varepsilon_r - \frac{j\sigma}{\omega\varepsilon_0})\mathbf{E} = 0 \tag{3}$$

where $\mu_r$is relative permeability, $\sigma$is conductivity, $\varepsilon_r$is relative dielectric

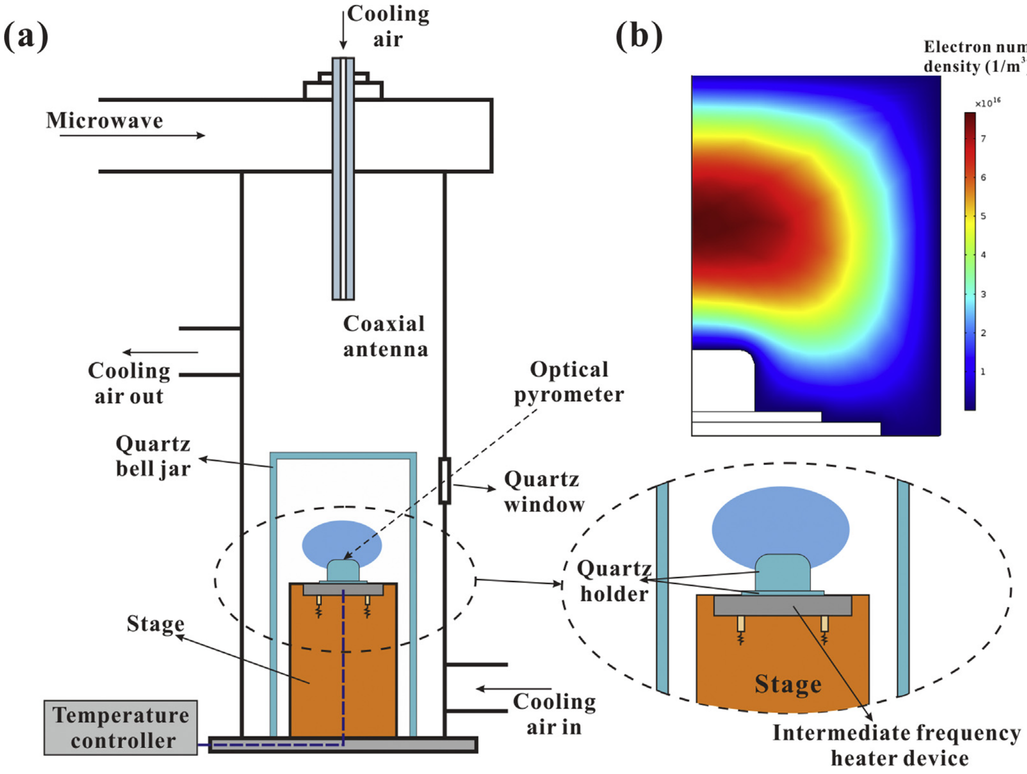

Fig. 1. (a) Schematic of the MPCVD with the quartz holder, of which the total height is about 14 mm, (b) simulation result about the distribution of Ar plasma electron density.