Modeling of a microwave induced plasma for (ultra)nanocrystalline diamond film deposition

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Abstract: In this paper, a hybrid plasma equipment model (HPEM) was applied to study a microwave induced plasma used for (U)NCD film deposition. Argon was used as the only feedstock gas in this study to investigate the fundamentals of an ASTEX 6560 microwave plasma assisted CVD system. The results show that a hemispherically shaped plasma is generated above the substrate holder, as observed in the experiment. The study of the excited Ar* flux suggests that a fairly uniform radical flux can be achieved in this CVD system, which will ensure the uniformity of the film during the deposition.

Keywords: modeling, hybrid model, microwave plasma, CVD, diamond film

1. Introduction

Ultrananocrystalline diamond (UNCD) and nanocrystalline diamond (NCD) films are attracting more and more interest due to their unique electrical, optical, and mechanical properties, which make them widely used for different applications: MEMS devices, high-temperature rectifying diodes, biosensors, thermoelectric, etc [1-4]. Compared to NCD films, UNCD films have much smaller grain sizes (~2-5 nm) and have little or no graphitic impurities at the grain boundaries. NCD films are usually synthesized in a H2 (99%) dominant CH4 (1%) microwave plasma [5], while UNCD films are synthesized in a moderate-pressure microwave discharge with a gas mixture of 1% CH4 in Ar, and usually with the addition of 1-7% H2 [6].

The ASTEX 6560 microwave plasma assisted CVD (MPACVD) reactor, as is shown in Fig. 1, is the newest developed microwave system produced by SEKI Technotron Corp. [8], which can accommodate a larger size of wafer such as 4 inch diameter. In such reactor, the microwave is guided into the chamber from the bottom side of the stage, and concentrated above the substrate holder on the stage. The distance between the substrate and the top-wall of the chamber is almost the same as the wavelength, ~12 cm for 2.45 GHz of frequency. Hence a standing wave like electric field forms and limits the vertical extent of the plasma.

In the past decades, intensive experimental and theoretical work has been carried out to reveal the underlying physical and chemical picture of (U)NCD film growth. However, the fundamental growth mechanism of these (U)NCD films is still unclear. It was initially suggested that the C2 radicals play an important role in the growth mechanism [7]. However, May et al. [6] proposed a new mechanism based on (i) the attachment of CHx species (x=0..3, specially C atoms) followed by local surface restructuring, (ii) the reduction of the efficiency of the β-scission reaction, or (iii) a combination of these two processes. During the (U)NCD film deposition, the growth rate and uniformity are determined by the flux of reactive species. However, according to authors’ knowledge, only a few works have been carried out on this topic in a microwave induced plasma for (U)NCD film growth.

The final aim of our work is to develop a model for a microwave induced plasma with an Ar/H2/CH4 mixture, which will be used for the deposition of (U)NCD films, in order to investigate the underlying chemical mechanisms. However, as the first step of this study, a hybrid model, called the hybrid plasma equipment model (HPEM) [9-15] is extended to investigate an argon discharge in the ASTEX 6560 MPACVD system. In the HPEM, the momentum equations for neutrals and ions are solved separately, which provides us an opportunity to obtain an insight in the behavior of the fluxes in the MPACVD reactor.

2. Description of the model and reaction mechanisms

The HPEM is a 2-D plasma equipment model devel-
oped by Kushner and co-workers [9-15], which can model complex reactor geometries and a wide variety of operating conditions. The HPEM allows for a variety of plasma heating sources and gas chemistries. The basic 2-D HPEM consists of an electromagnetic module (EMM), an electron energy transport module (EETM), an electron Monte Carlo simulation (EMCS), and a fluid kinetics module (FKM).

Recently, a full-wave Maxwell solver is developed by Yang [16] to investigate the wave effects in 2-frequency capacitively coupled plasma (CCP) tools. The total electric field is separated into two components: electromagnetic (EM) part and electrostatic (ES) part. For the EM component, the TM mode is excited in cylindrical geometry and gives $E_r, E_z, H_\theta$, which is solved using finite-difference time-domain (FDTD) techniques with the Crank-Nicholson scheme on the staggered mesh:

$$\frac{\partial E_r}{\partial Z} - \frac{\partial E_z}{\partial r} = -\mu_0 \frac{\partial H_\theta}{\partial t}$$

$$\frac{\partial H_\theta}{\partial Z} = J_r + \varepsilon_0 \frac{\partial E_z}{\partial t}$$

$$1 \frac{\partial (rH_\theta)}{\partial r} = J_z + \varepsilon_0 \frac{\partial E_r}{\partial t}$$

(1)

where $\mu$ and $\varepsilon$ are the permeability and permittivity respectively, $J$ is the electron current calculated from the drift-diffusion approximation. The ES component is obtained by solving Poisson’s equation semi-implicitly.

$$\nabla \cdot (\varepsilon \nabla \Phi(t + \Delta t)) = \rho(t) + \frac{d\rho(t, \Phi(t + \Delta t))}{dt} \Delta t$$

(2)

Then the sum of the EM and ES part is executed for plasma transportation. In order to simulate a microwave plasma reactor, a slight change about the boundary condition for Eq. (2) has been made: in a 2-frequency CCP simulation, a large DC voltage should be applied on the surface of the substrate holder, because the substrate was connected with an RF generator through a small electric capacity, while in a microwave discharge, only a small DC voltage appears.

| Table 1: The species and chemical reactions considered in the simulation |
|-----------------------------|------------------|------------------|------------------|
| Species | $Ar, Ar^+ (n=2, 1P_2, 3P_{0,1,2}), Ar^+, e$ |
| Reactions | $e + Ar -> Ar + e$ | $e + Ar -> Ar^+ + e$ | $e + Ar -> Ar^+ + e + e$ |
| | $e + Ar^* -> Ar + e$ | $e + Ar^* -> Ar^+ + e + e$ | $e + Ar^+ -> Ar$ |
| | $Ar^* + Ar^* -> Ar^+ + Ar + e$ | | |

Fig. 2 Calculated the electric field in the resonance cavity without plasma a) $E_r$ and b) $E_z$ as well as with plasma c) $E_r$ and d) $E_z$. 
Briefly, continuity, momentum, and energy equations for neutrals and ions; continuity and energy equations for electrons and a full-wave Maxwell solver are integrated in time to obtain a periodic steady state. More details about the Maxwell solver can be found in [16].

In this study, as a first step the investigation is conducted using only argon as the feedstock gas. The species and reactions mechanisms are listed in Table 1, where Ar* \((n=2, \, ^1P_1, \, ^3P_0,1,2)\) represents the excited state including the metastable and resonance states of Ar. An argon gas flow of 200 sccm is introduced from the top-wall of the chamber toward the substrate, and the input power and gas pressure were fixed as 400 W and 1 Torr, respectively.

3. Results and discussion

Fig. 2 show the calculated EM field in the whole reactor without plasma in a) and b), as well as with the argon plasma in c) and d); the unit is V/cm. Without the plasma a standing-wave structure can be observed, and the distance between the maximum and minimum values is close to the half wavelength ~ 6 cm. The strongest electric field is just formed above the substrate holder as expected. We can also see that the electric field exhibits a peak at the corner of the stage and the reactor due to the point discharge.

With the plasma, the field strength above the substrate holder decreases since the EM energy is absorbed by the plasma, and the standing-wave like structure becomes less pronounced in the vicinity of the plasma. Hence, the behavior of the EM field is totally modified by the plasma.

The two-dimensional profiles of electron density and gas temperature are shown in Fig. 3 a) and b), respectively. The gas pressure is 1 Torr and the input power is 400 W. It is clear that a hemispherical plasma forms above the substrate holder, exactly as expected. The electron density exhibits a peak of 2.8x10^{11} cm^{-3} at the center of the reactor around 0.9 cm above the substrate holder, and de

![Fig. 3 Two-dimensional profiles of a) electron density and b) gas temperature, for a pressure of 1 Torr and a power of 400W.](image)

![Fig. 4 Two-dimensional profiles of a) radial and b) axial components of the Ar* flux as well as c) the Ar* number density.](image)
creases one order at the edge of the plasma ball. It also shows to be fairly uniform in the radial direction in the neighborhood of the substrate holder.

The distribution of gas temperature is shown in Fig. 3(b). An off-axial peak of 508 K is observed around 2 cm above the substrate holder, whereas another peak is found at the corner of the substrate holder. Fig. 4 shows the two-dimensional profiles of the excited Ar* \((n=2, \, ^1P_1, \, ^3P_{0,1,2})\) flux with a) radial and b) axial components, as well as c) the corresponding number density. We can find from Fig. 4 c) that the excited Ar* atoms are characterized by a similar distribution as the electrons, and reach a density as high as \(10^{12} \text{ cm}^{-3}\) above the substrate holder. In the region above the substrate, the Ar* flux is fairly uniform in the radial direction, while in the axial direction, the flux exhibits local maxima of \(10^{15} \text{ cm}^{-2} \text{ s}^{-1}\) at about 4 mm above the substrate. These results suggest that a uniform film can be deposited in such reactors. In addition, a very strong Ar* flux is found at the corner of the substrate holder, which could cause sputtering from the holder and should be avoided.

4. Conclusions and outlook

The HPEM was developed to simulate a microwave induced plasma for (U)NCD film deposition. As the first step of our work, an argon plasma at a pressure of 1 Torr is simulated in this study. The results are consistent with known experimental results. The distribution of the Ar* atom flux suggests that a uniform film can be deposited in this kind of microwave reactor.

Due to limitations of the HPEM, the simulation can only work under low pressure (below 10 Torr), and this limitation will be solved in future work. In addition, in future work, the model will be extended to an Ar/H\(_2\)/CH\(_4\) plasma and the effects of source power, gas pressure and gas mixing ratios on the plasma characteristics and on the densities and fluxes of plasma species above the substrate will be investigated.

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References