Diamond & Related Materials 54 (2015) 9–14

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Numerical microwave plasma discharge study for the growth of large single-crystal diamond

Hideaki Yamada *, Akiyoshi Chayahara, Yoshiaki Mokuno, Shinichi Shikata

Research Institute for Ubiquitous Energy Devices, National Institute of Advanced Industrial Science and Technology, 1-8-31 Midorigaoka, Ikeda, Osaka 563-8577, Japan

ARTICLE INFO

Available online 15 November 2014

Keywords:
Microwave plasma CVD
Diamond
Simulation

ABSTRACT

A microwave plasma discharge simulation was conducted to determine the spatial concentrations of hydrocarbon radicals and their uniformity over areas over 25 mm^2. Dependences of these on controllable growth parameters were also determined. Parameters included the absorbed microwave power, the methane concentration in the feed gas mixture and the gas pressure. The radical concentrations that were obtained using simplified chemistry for the source gas species are consistent with those specified in other reports. The radical concentrations were consistent with the experimental growth rates but not with their distributions. This suggests the importance of substrate temperature uniformity and a contribution from $CH_x (x < 3)$ in addition to CH_3.

1. Introduction

Diamond is a gemstone, and a material with several extreme characteristics that are superior to those of other materials [1]. Single-crystal diamond (SCD) possesses characteristics such as a wide bandgap, high carrier mobility and high thermal conductivity. These make it a promising candidate material for use in devices such as high frequency and high power electronics that require characteristics superior to those of conventional materials [1,2]. Synthetic diamonds were first produced by a high temperature high pressure (HPHT) method [3]. This method has been used to fabricate diamond particles and powders mainly for mechanical use. Microwave (MW) plasma chemical vapor deposition (CVD) can also be used to grow diamonds in the vapor phase [4]. This method is currently widely used to fabricate semiconductor grade SCD [5–8].

For the industrial use of diamonds in electronics, the fabrication of large wafers of sufficient quality is required for acceptable device performance and with acceptable cost. HPHT cannot be used for this purpose because of the scale of the apparatus. Crystals of several inches in diameter have not been produced using this method. In contrast, plasma CVD is a relatively easy method wherein the deposition area can be relatively high. For the plasma etching of Si wafers in the semiconductor industry a 450-mm-diameter wafer size has been achieved [9]. For SCD, plasma CVD is used to grow thin-layer and bulk crystals [4–8,10–14], as mentioned above. The typical seed substrate size of several millimeters is much smaller than the MW wavelength of approximately 12 cm, and not much attention has been given to uniformity to date.

New techniques to increase the size of seed crystals have been reported [10,15] and it has been shown that a 40 × 60 mm^2 wafer can be fabricated using this technique [16]. For crystal growth on such a large wafer where the wafer size is comparable to the half-wavelength, nonuniformity becomes important [16,17]. To improve the uniformity and to deliver a high growth rate, it is important to understand the global distribution and the dynamics of the precursors for diamond growth over a large area. Numerical simulation is a powerful tool to study this growth because conventional measurements have hardly been applied to plasma discharge for diamond growth. The gas pressure is typically high and the gas temperature is extremely high. Several studies have investigated radial dynamics in the gas phase [18–20] as well as surface reactions [21,22] to predict the growth rate and to understand their relationship with quality. However, the dependence of uniformity in the horizontal direction on several growth parameters is still not understood.

To investigate specific factors that affect these uniformities, we conducted two- and three-dimensional numerical simulations of MW plasma discharge. We studied the dependence of radical concentrations and their distribution in the horizontal direction on several discharge parameters. The calculated results allow for an estimation of the growth rate distribution [21,22]. In this manuscript, we considered the potential of the current MW plasma CVD method for the growth of SCD with large areas.

2. Calculation procedure

The calculation procedures are briefly described below and further details may be found in Ref. [25] and the references therein. Because the Knudsen number is low, we adopted a fluid based model [20,23–25]. The procedure consisted of two calculations: a calculation to solve the Maxwell equations, which are coupled with the reduced transport

* Corresponding author.
E-mail address: yamada-diamond@aist.go.jp (H. Yamada).

http://dx.doi.org/10.1016/j.diamond.2014.11.005
0925-9635/

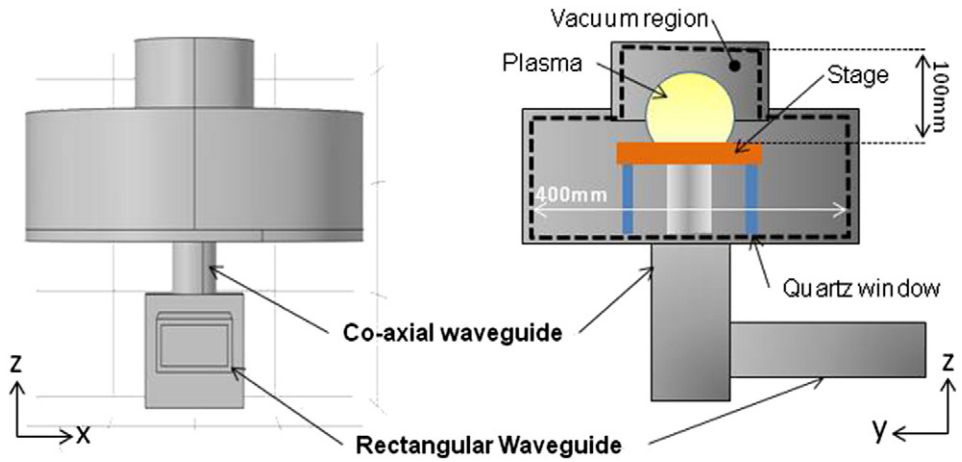

Fig. 1. Schematic of the calculation domain; (left) outer boundary, (right) interior region.

equation for electrons [23], and a calculation to solve the transport equations for the source gas mixture [24,25]. From the first calculation we obtained the electromagnetic field distributions, the electron number density and the power density. The second calculation was used to obtain subordinate solutions of the source gas mixture.

For diamond growth, the gas pressure and the temperature are typically $\geq$0.1 atm and $\leq$3500 K, respectively. In this situation the excited source gas molecules/atoms are immediately de-excited because the relaxation time periods of the excited species are much shorter than the excitation periods [23,25]. Therefore, the MW power that is absorbed by the electrons is transferred to the translational modes of the source gas molecules/atoms locally [23]. As suggested in other literature [18,20] the thermal dissociation of the source gas molecules/atoms is dominant compared with electron impacts. Therefore, we only used the power density distribution of the first calculation as a heat source for the second, source gas mixture calculation.

For source gas mixture calculation, the kinetic diffusion model was taken into account for the viscous force [24,26] where Lennard–Jones (L–J) potentials were used to specify the viscous force. Details about the governing equations are given in our previous work [24,26–28]. For simplicity, constants in the L–J potentials of all the hydrocarbon molecules were set to those of CH_4 and CH_3. Material constants such as molar enthalpy and entropy were obtained from the literature [29]. The molecule/atom chemistry was based on an open set of chemical kinetics [30]. The chemistry used in this work is simpler than that used by other groups [18–20]. While the predominant reaction mechanism for diamond growth is still not clear, as discussed in the following sections, the obtained results are consistent with those reported in the literature. The boundary conditions of the source gas molecules/atoms were determined by considering the molecular dynamics simulation results and known absorption coefficients [31–33].

Fig. 1 shows the calculation domain in which the actual experimental setup was reproduced [34,35]. A Mo substrate holder disk with a diameter of 60 mm and a thickness of 10 mm was placed at the center of the stage with a diameter of almost 200 mm. A circular hollow with a diameter of 50 mm and with a holder top thickness of 3 mm was used. A diamond wafer 50 mm in diameter and 3-mm thick was placed on this hollow on the substrate holder for the calculation. The electron

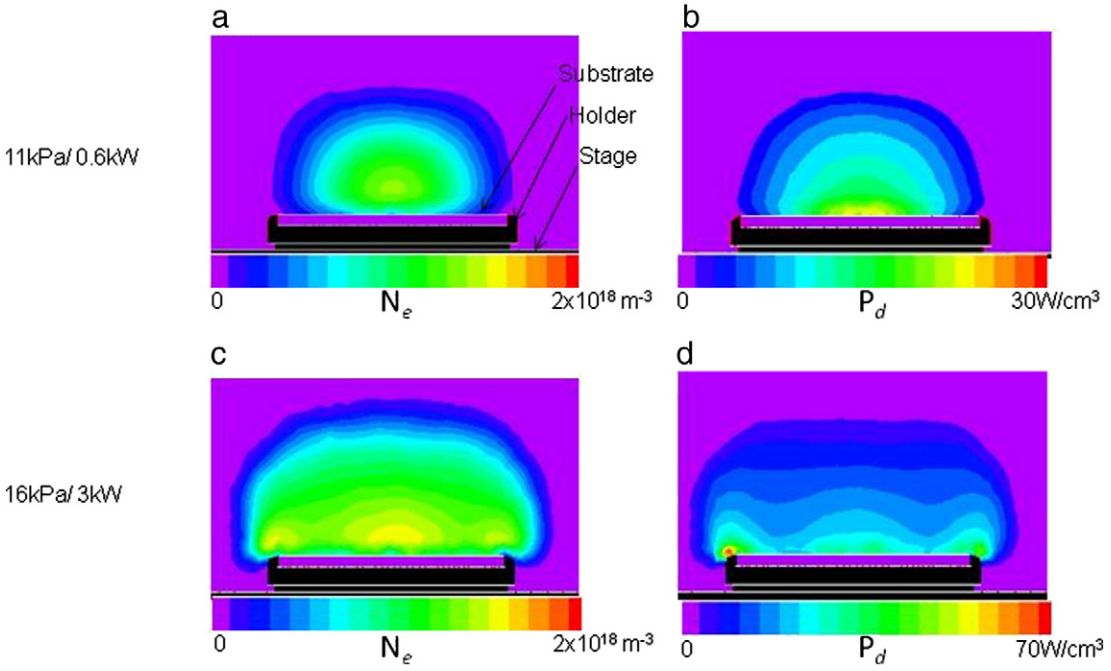

Fig. 2. Cross sectional distributions of the electron number density and the power density. The results shown are (a) electron number density obtained under gas pressure 11 kPa and MW power 0.6 kW, (b) power density obtained under gas pressure 11 kPa and MW power 0.6 kW, (c) electron number density obtained under the gas pressure 16 kPa and the MW power 3 kW, and (d) power density obtained under the gas pressure 16 kPa and the MW power 3 kW.