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Species with nitrogen in Microwave plasma discharge for synthesis of single crystal diamond

MWPCVDによる単結晶ダイヤモンド合成時の窒素を含む化学種

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Simulation of microwave plasma discharge, whose condition is adjusted for synthesis of single crystal diamond, has been conducted. Chemistry which includes nitrogen as well as hydrocarbon species is taken into account for the first time. Transport equations of constituent species as well as electrons are solved with Maxwell Eqs. quasi-consistently by using a fluid base model. Obtained results are compared with some preceding results, and we found that these are in good agreement with each other.

1. Introduction

Improvement of power efficiency is one of the keys to save limited energy resources and realize sustainable economic activity. For example, automotive semiconductors made of SiC may not need additional cooling system and its system may be able to be simplified compared with those made of Si [1]. This is one of the reasons why the wide-band-gap materials, where SiC is also one of them, have been extensively studied. Among such wide-band-gap materials, single-crystal-diamond (SCD) is also known to be a promising material, which has several characteristics superior to those of others [2]. Nowadays, several researchers have demonstrated improved device/system performance by using SCD [3].

One of the big issues for realization of its industrial use is their wafer sizes and qualities. Commercially available size of SCD is several millimeter square today. Further, control of densities of impurities and defects are severer because they directly affect on device characteristics. Authors have studied and developed techniques to solve these issues [4-5]. Under relatively high-gas pressure with introduction of small amount of nitrogen, Dr. Mokuno, et al. have succeeded in continuous growth of SCD and fabricating half-inch (≈13mm) size free-standing wafers of SCD [5]. Nitrogen has some important roles during such growth, e.g. stabilization of a certain crystallographic surface and increase of the growth rate [4]. Further, doping of such impurity causes lattice mismatch and internal stress inside the crystals. Because subtle change of the growth condition alters results, such as the incorporation of nitrogen into the grown crystal in such growth environment, as suggested in several literatures [4, 6, 7], it is important to understand the mechanism and control their activity during the growth. On the other hand, under the condition here, it is not easy to measure plasma parameters during the growth.

From above reasons, we have conducted numerical simulation and modeling which is necessary to conduct calculation [7-9]. Several research groups have tried such simulation [10, 11]. However, they just conducted calculations for pure hydrogen system or H_2/CH_4 system, but do not introduce impurity in the system. In this paper, preliminary results in which nitrogen is introduced into the system for the first time.

2. Modeling

The calculation was conducted under the system which is the same with those adopted in Ref. 9. Feedstock gas consists of H_2, CH_4, and N_2 as in experiments. Mass flow rates (MFRs) of them are set to H_2:CH_4:N_2=500:25:5sccm respectively. MFR of CH_4 is similar to those of Refs. 10 and 11. MFR of N_2 is relatively larger than those in experiments [5] because of hardness to obtain converged solutions for MFR much smaller than that adopted here. Gas pressure is kept 16kPa (120torr) and microwave power absorbed by plasma here is 3kW. As shown in Ref. 9, dynamics of electrons coupled with electromagnetic field is calculated first. Then, dynamics of feedstock gas is calculated under the power density which is obtained in the preceding part of the calculation. This procedure is considered to give appropriate solutions under the situation in some extent, where the gas pressure is relatively high and the most of the feedstock gas is only one species [8]. While the chemistry is simplified in the previous works [7-9], variety of species and chemical reactions among them are taken into account in this work, which is based on the open source of the chemistry database [12].

3. Results

Figures show contours of various quantities in a cross section of the apparatus, where distributions at region above the substrate are presented.

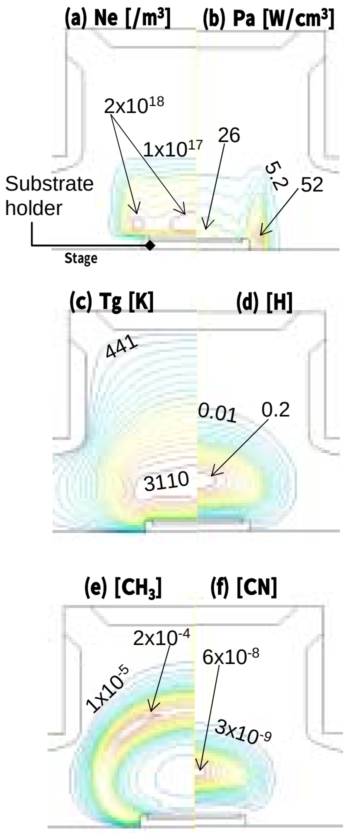

Figure. Sample results (See text about the conditions)

Figures (a) and (b) show distributions of electron number density and power density, respectively. Plasma is concentrated only around the substrate holder. Gas temperature is shown in Fig. (c), where its maximum value is around 3000 deg. C. Figure (d) shows mole-fraction of H. Because thermal dissociation is dominant under the condition here [10], its profile is similar to that of the temperature. Due to the recombination with H and diffusion effect, CH_3 shows shell-like structure [Fig. (e)]. On the other hand, distribution of CN is similar to that of H, i.e. gas temperature [Fig. (f)].

Comparing with the case w/o nitrogen [9], introduction of small amount of N_2 does not cause significant change on the distributions of the temperature and H, which is also expected from OES measurements in actual experiments. Further, those values obtained here is similar to those obtained by using simplified chemistry [9], while distributions of CH_3 is different because of complex reaction paths among hydrocarbons.

In Ref. 10, results obtained for 12kPa/2kW/H_2:CH_4=95:5 where 200 sccm in total are shown for a different type of the reactor configuration. All of magnitudes as well as distributions given here is in good agreement with those shown in Ref. 10. This is because the conditions are close to each other and plasmas are concentrated only around the substrate in both cases while the reactor configurations are different from each other.

4. Summary

Simulations of microwave plasma discharge in which N_2 as well as H_2/CH_4 are introduced in a feedstock gas have been conducted. Comparison with the previous works show good agreement with each other, which also supports validity of some assumptions in the chemistry and the calculation procedure here. Nitrogen containing radicals such as CN is shown for the first time. Introduction of small amount of nitrogen does not cause significant change on the distributions of temperature and species without nitrogen. Further detailed study may reveal mechanism of incorporation of nitrogen into the substrate during the growth of SCD.

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