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Map of growth rate of diamond film synthesized by use of flame CVD

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Abstract

Optimum conditions for the flame synthesis of diamond films have been studied by examining effects of the equivalence ratio, ejection velocity, and velocity gradient on the growth rates and morphologies of diamond films. Important factors that can affect growth rates and morphologies of diamond films deposited in the flame are confirmed to be temperature, flow, and species concentration fields. By use of a flat flame burner, these influences are well understood because the flat acetylene/hydrogen/oxygen flame is stabilized in a well-defined stagnation flow field, which can be regarded as one-dimensional field. It is found that the maximum growth rate can be obtained when the equivalence ratio is from 2.45 to 2.50. It has also been confirmed that the growth rate is nearly the same when the velocity gradient is kept constant. This result indicates that the velocity gradient is one of the important parameters that can govern the growth rate of diamond film. Furthermore, in order to obtain universal, optimum conditions for the flame synthesis of diamond films, an attempt has been conducted to make a map of the growth rates, as functions of equivalence ratio and velocity gradient. Although growth rates increase with increasing velocity gradient, excessively high velocity gradients cause decrease in growth rates. It is found that the maximum growth rate can be obtained when the equivalence ratio is around 2.50 and velocity gradient is 4000 s^{-1}.

Keywords: Diamond synthesis; Flame CVD; Stagnation flow field; Velocity gradient; Map of growth rate

1. Introduction

It has been well recognized that diamond is one of the most valuable materials in future industries, because of its highest hardness, Young's modulus, thermal conductivity, and so on. It has good chemical, electrical, and optical properties [1,2], too. Especially, diamond semiconductor [3] is strongly expected to be used in practice because of its high band-gap of 5.45 eV. Furthermore, diamond films synthesized by use of chemical vapor depositions (CVD) are considered to have the possibilities of practical applications expanded.

Among various CVD methods, the flame CVD [4] has been recognized as a rapid technique to produce high quality films. It was reported that the growth rate of the diamond films is 100–150 μm/h [4] and that good quality diamond with optical transparency can be

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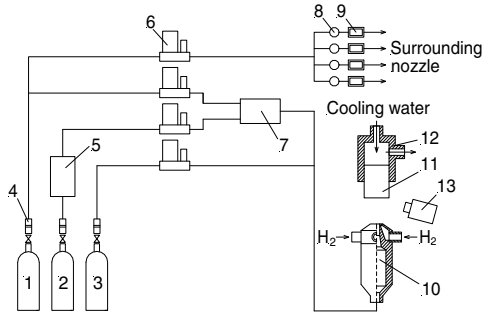
obtained [5]. The most attractive advantage of the flame CVD is that it can synthesize diamond films under atmospheric environment, whereas other CVD methods need low-pressure environments, so that what are required for the flame CVD are basically an oxyacetylene burner and a substrate. Because of its simplicity, the flame CVD method has attracted special attentions from many researchers. Since Hirose et al. showed synthetic ranges for diamond films as functions of the equivalence ratio of oxyacetylene flame and/or the substrate temperature [5], the elucidation of the synthetic ranges has been one of the main research subjects in this research field [6–9]. Besides, to improve quality and deposition area, a low-pressure flame CVD has been conducted [10]. An addition of very small amount of nitrogen has also been reported to increase growth rate [11]. Laser diagnostics [12,13] and mass spectrometry [14] have even been used to analyze species concentrations in the flame. Numerical studies [6,12,15–17] further revealed that CH_3, C_2H_2, H and/or some other radicals play important roles in flame synthesis of diamond films. An attempt was also made to synthesize large single crystals using flame CVD method [18], reporting that large single crystals (80–90 μm diameter) can be obtained by virtue of negative bias application on the substrate during the synthesis. In addition, an effort to make high quality diamond films for applications in electronic devices has been made [19].

Most experiments, however, have been conducted by use of conical flames, so that the combustion field necessarily becomes complicated, and hence it becomes difficult to identify dominant parameters for the synthesis. Generally applicable results for all flame CVD methods have not been obtained yet. As for a flat flame burner, developed by Murayama and Uchida [20], it can be considered to be an appropriate tool in obtaining and/or investigating universal conditions for synthesis, because it can offer a well-defined, one-dimensional stagnation flow field. In addition, it is considered to be of great use in scaling up deposition area.

In the present study, usefulness of flat flame has first been reconfirmed by comparing deposition area and growth rates, synthesized by use of the flat flame burner and the welding torch. After that, effects of equivalence ratio, ejection velocity, and velocity gradient on the growth rate and/or morphologies of the diamond films, synthesized by use of the flat flame burner, have been examined. Furthermore, in order to obtain universal, optimum conditions for the combustion synthesis of diamond films, an attempt has been conducted to make a map of growth rate, with respect to the equivalence ratio and velocity gradient.

2. Experimental

A schematic diagram of the experimental setup is shown in Fig. 1. Acetylene, oxygen, and hydrogen are supplied from cylinders with the purities 99.6%, 99.5%, and 99.9%, respectively. An activated carbon filter is installed in the acetylene line to remove dimethylformamide solvent containing in acetylene gas. The flow rates of the gases are controlled by mass flow controllers (Brooks 5850E and Kofloc 3610). A flat flame burner under a stagnation flow is intensively used in this work to establish uniform temperature and species concentration fields. The flat flame burner, being manufactured, based on studies by Murayama and Uchida [20], consists of a main nozzle (2 mm diameter) and a surrounding nozzle (3.5 mm diameter), mainly. A flat, premixed, acetylene/hydrogen/oxygen "inner" flame, indispensable in synthesizing diamond films, can be established in front of a substrate, by virtue of the co-axial flow with hydrogen, ejected from the surrounding nozzle. A molybdenum substrate, a rod of 15 mm in diameter and 20–35 mm in length, is set in a water-cooled holder. The deposition surface of the substrate is scratched, prior to each experimental run, using a SiC emery paper with a slurry of Al_2O_3 powders (15 μm) and distilled water, and then cleaned with ethanol. The surface roughness (Ra) is set to be 0.15 μm for each experimental run. The substrate temperature T_S is measured by means of an infrared radiation thermometer (CHINO IR-AP2CPR) with the thermal emissivity set to be 0.7 [20]. In this work, the substrate temperatures are set to be around 940 K, following to the Authors' previous results that the growth rate decreases in the temperature range form 1000 to 1100 K, in spite of an increase



1. Hydrogen
2. Acetylene
3. Oxygen
4. Flashback arrestor
5. Activated carbon filter
6. Mass flow controller
7. Mixing chamber
8. Needle valve
9. Mass flow meter
10. Flat flame burner
11. Molybdenum substrate
12. Substrate holder
13. Infrared radiation thermometer

Fig. 1. Schematic diagram of the experimental setup.