Journal of Korean Association of Crystal Growth
Vol. 8, No. 2 (1998) 227-232

Synthesis of diamond thin films by hot-filament C.V.D

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Hot-Filament 화학증착법에 의한 다이아몬드 박막의 생성에 관하여

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Abstract Diamond crystallization and discontinuous deposit phenomena depend on the process of hydrocarbon deposition, nucleation and growth. Then, it is investigated the concentration of methane, flow rate, structure and the growth process of CH_4-H_2 system in hot filament assisted C.V.D. There is a limited value of temperature, pressure, flow rate and the mole fraction of methane-hydrogen gas. Diamond nucleation occurs on substrate selectively and surface diffusion of species on the substrate plays an important role in the early stages of nucleation and growth.

요 약 Si, Mo 등을 substrate로 하고 Hot-Filament C.V.D법으로 저압에서 다이아몬드 박막을 생성시킬 때 탄화수소의 부착과정, 핵생성 및 성장을 조사하였다. 특성은 substrate의 종류, 온도, 압력, 유속 및 CH_4-H_2가스의 몰분율과 같은 process변수로 조사하였으며 다이아몬드는 Raman spectroscopy로 측정하였다. 특히 다이아몬드 핵생성과 성장은 scratch와 같은 결함이 있는 곳에 발생하였고 표면확산 등이 핵생성 초기단계에서 중요한 역할을 하였다.

1. Introduction

The combined superior electronics, optical and tribological properties of diamond makes it an attractive material, it is made in the thermodynamic stability region of HPHT (high pressure and high temperature) and in the thermodynamically low pressure region. During the past few years, significant progress [1-3] in hindered region has been made on various techniques (hot filament, microwave, plasma, RF, combustion, laser, ion-beam etc), but further development is hampered by fundamental mechanistic understanding.

In general, diamond film by low pressure chemical vapour deposition is considered on 2 parallel process of chemical processes which are involved in continuous reaction between gas phase reactants and physical process related to adsorption, surface migration, nucleation and growth. Therefore, the effects of various parameters such as temperature, time, supersaturation, substrate composition, atomic hydrogen and flow rate are very important in order to understand the relationship of processing, structure and property in these complex material systems. That is, a characteristic of gas phase synthesis is excited carbon atoms by dissociation of a carbonaceous compound and thermodynamic conditions in the synthesis are favorable for graphite and diamond is only metastable. Hence, codeposition of nondiamond carbon has to be suppressed by atomic hydrogen presented excessively in the reaction chamber [4]. Then, in this study, the effects of substrates surface and treating conditions such as temperature, time, filament-substrate distance and flow rate are examined in order to investigate the nucleation phenomena for a given substrate mode with cooling wall which gas ambient is closer to the thermodynamic equilibrium.

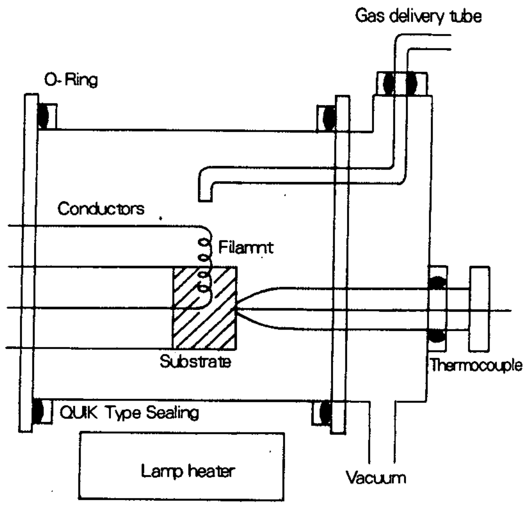


Fig. 1. Schematic diagram of hot-filament assisted C.V.D. diamond apparatus.

2. Experiment

As shown in Fig. 1, diamond nucleation and growth is carried out in a quartz reaction chamber on a substrate beneath a hot filament (tantalum or tungsten) at low pressure. Substrate was not biased. Pressure was 20-50 torr, and substrate to filament distance was maintained at 5 mm. Specimens were rinsed in methanol after scratch the surface with diamond abrasive powder. Graphite was used to substrate holder attached to the thermocouple, which is good heat sink. The pressure and filament temperature were adjusted and stabilized in hydrogen prior to introducing the CH_4-H_2 gas. We surveyed optical microscopy, SEM in order to observe the nucleation and growth and used X-ray diffractometer, Raman spectroscopy for the purpose of investigating composition, orientation and quality.

3. Results and Discussion

The gas phase chemistry [5] is important, since it establishes the concentration of carbon available at the surface of the substrate. Moreover, atomic hydrogen is responsible for the preferential etching of graphically bonded carbon over that of diamond bonded carbon. Major regarding the diamond synthesis at low pressure will be mole fraction of gas phase, temperature, pressure, pre-treatment of substrate, substrates of molybdenum and silicon to a variety of chemical, mechanical and physical process prior to similar exposure in a hot filament chemical vapor deposition reactor. The reaction project was obtained on the substrates as particles up to 4 μm in size. Raman spectra of these specimens (Fig. 2) showed a sharp peak at 1334 cm^{-1} which is very close to the value of 1332.5 cm^{-1} reported for natural diamond. Vickers hardness of the films formed by hot-filament C.V.D whose thickness is 2-4 μm is about 8500 kg/mm^2 for 400 grams of load. This value is the same as that of the natural diamond (7000-10000 kg/mm^2). Figure 3 shows the nucleation and growth process CH_4-H_2 system in filament assisted C.V.D.

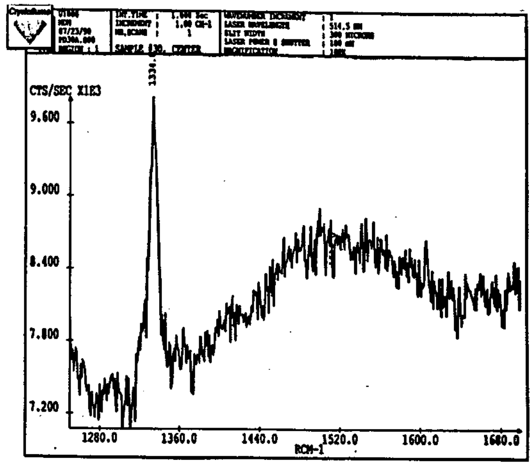


Fig. 2. Raman spectroscopy typical of diamond peak near 1332 cm^{-1}.

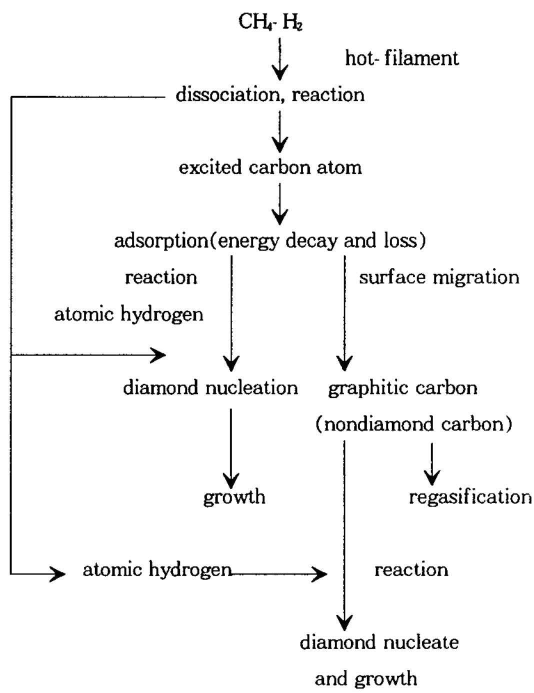


Fig. 3. Growth process of CH_4-H_2 system in filament assisted C.V.D.

Methane-Hydrogen mixture on filament is changed into hydrocarbons [6] such as

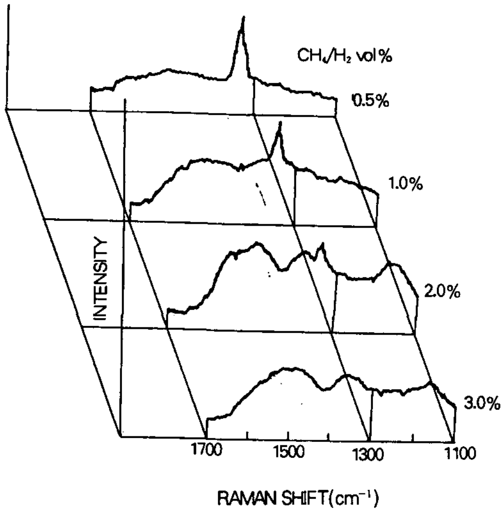


Fig. 4. Raman spectra of diamond films for different methane concentrations.

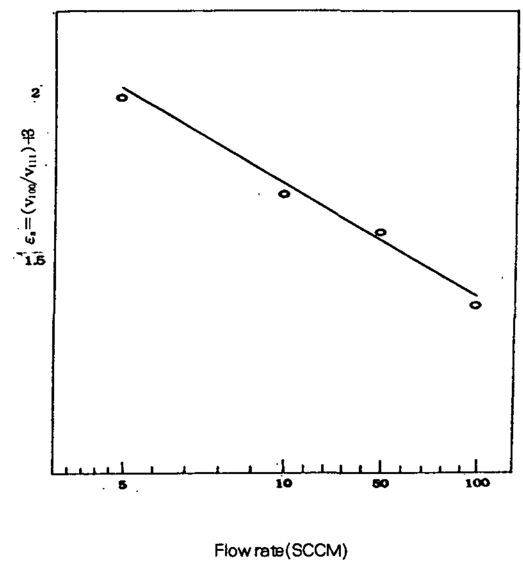


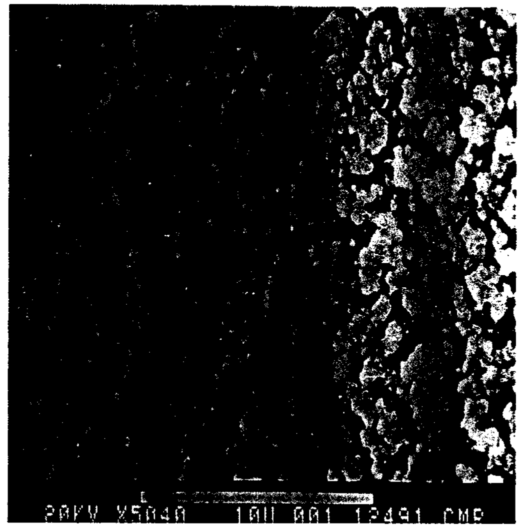
Fig. 5. Effect of flow rate 950℃ under 33 torr in methane (1%)-hydrogen gas.

CH_3, C_2H_4, C_2H_2 by decomposition and reaction. Active carbon atoms by decomposition of hydrocarbons on substrate and excited carbon atoms by hot filament produced [7] the formation of diamond nucleation. Hydrogen atoms varied significantly with the reactant CH_4/H_2 fraction as well as with the filament temperature. That is, thermodyna-mic conditions in the synthesis are favorable for graphite and diamond is only metastable [8]. Therefore, co-deposition of nondiamond carbon has to be suppressed by atomic hydrogen excessively presents in the reaction chamber. Besides, it can be considered the maintenance of a hydrogen terminate on substrate and abstraction of chemisorbed hydrogen to create reaction sites on the diamond surface. Figure 4 shows the effect of methane concentration, which is Raman spectra of diamond films for different methane concentration. The Raman spectra notes prominent diamond peak near 1332 cm^{-1} under 1 % CH_4. Peak disappears as the methane concentration increases over 1 % CH_4. This is due to the formation of amorphous structure of carbon atoms.

Figure 5 shows the effect of flow rate of 950℃ under 33 torr in methane(1 %)-hydrogen gas. In this experiment, facet decreased as flow rate increase. Moreover, diamond particle with defined habit is not represented at 150 sccm. This fact shows high flow rate results in the formation of graphitic carbon related to diamond nucleation on substrate surface. Figure 6(a) is the SEM of the deposites on Mo substrate at temperature 1173 °K, flow rate 50 sccm, pressure 33 torr and a CH_4 concentration of 1 vol% formed by hot-filament

(a)

Fig. 6(a). The SEM image of the deposites on Mo substrate.
Substrate temperature : 900℃
Filament temperature : 2000℃
CH_4 concentration : 1 vol%
Total flow rate : 50 sccm
Pressure : 33 torr



(b)

Fig. 6(b). The SEM image of the deposites on Mo substrate.
Substrate temperature : 600℃
Filament temperature : 2000℃
CH_4 concentration : 1 vol%
Total flow rate : 50 sccm
Pressure : 33 torr

thermal C.V.D for 10 hr. This shows clustering of diamond and same morphology represented on Si substrate under similar condition. From Fig. 6(a) and other experiment [9,10], it can be considered that nucleation occurred selectively and clustering of nucleation of nuclei is probable of surface diffusion on the substrate plays an important role in the early stages of nucleation and growth. Figure 6(b) is the SEM of the deposites at substrate temperature 773 °K under same condition. Surface was received scratch pre-treatment with diamond powder (3-4 μm). Samples were stripped in buffered oxide etch and rinsed in deionized water before processing. It shows low substrate temperature results in the formation of non diamond components, including microcrystalline graphite carbon and armorphous carbon. Figure 7 shows a nucleation line on molybdenum foil, which was scratched with diamond powder. In general, not all scratch are equal, and deeper scratches do not necessarily mean stronger nucleation, but it has been argued that an increase in the number of dangling substrate bonds at a nucleation site enhance nucleation such as Rabi and Koch have demonstrated that supplying a high surface defect density as well as a supply of

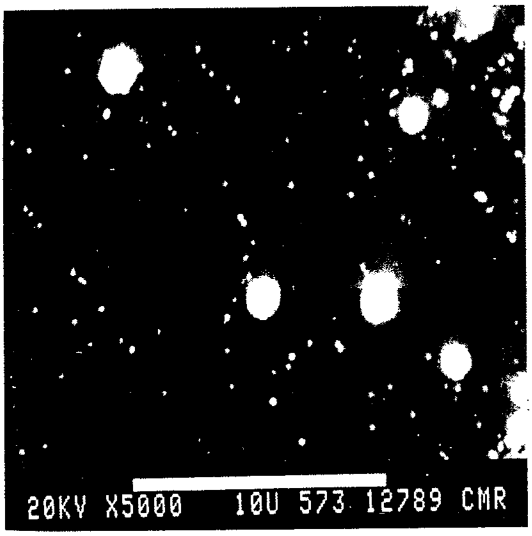


Fig. 7. A nucleation line on molybdenum foil.

hydrogen can lead to increased nucleation rate.

4. Conclusions

We investigated the influence of surface pre-treatment, gas composition and temperature on the nucleation and growth of diamond fibers on Si and Mo substrates from CH_4/H_2 in HF C.V.D. In low flow rate (about 50 sccm) and low pressure about (30 torr), 0.5 vol%CH_4 was the optimum concentration for producing well faceted diamond. Substrate surface scratched with abrasive powder was prominent for increasing nucleation and growth in early stage. Morphology of nucleation on Si substrate is the same as that of Mo substrate.

Acknowledgement

I extend thanks to several parties for helpful discussion and with facilities support from STANFORD, department of materials science and engineering : David A. Stevenson and Paul A. Denning (The present research was conducted by the research fund of Dankook University).

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