

MINIREVIEW ARTICLE

**Basic Principles of Growing Single-Crystalline
Diamond Films**

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ABSTRACT

Single-crystalline growth of diamond film is reviewed. The variations in chemical vapor deposition are discussed. In addition, the varying conditions of growth to obtain the optimum diamond films such as type of etching substrate, gas composition, temperature and pressure are compared. Finally, the characterization of the diamond films by several techniques such as Raman spectroscopy, scanning electron microscopy and X-ray diffraction are reviewed.

Keywords: Diamond film, single-crystalline, chemical vapor deposition

INTRODUCTION

Diamond is the hardest material and has the highest thermal conductivity among all known materials. Because of its hardness, diamond is far more effective than other competing materials used as abrasive, shaping, cutting or finishing tools. Its very high thermal conductivity makes it ideal for spreading and conducting the heat out of compact, high power, high speed electronic packages. It is also a promising candidate as a heat sink in high-power semiconductor devices and medium-wave oscillators. However, because of the high price of natural diamond, diamond films must be synthesized to provide cost effective materials. Synthetic diamond was traditionally produced by high pressure and high temperature techniques. In this paper, the fabrication and characterization techniques for single-crystalline diamond film are described.

Reports on The Fabrication of Single-Crystalline Diamond Films

Diamond film can be deposited onto insulator substrates by a d.c.glow discharge chemical vapor deposition (CVD) [1]. Two electrodes, a flat cooled cathode and a grid anode, were made from molybdenum and the gap between them was 17 mm. The substrate holder was insulated from the anode. The anode was modified in order to insulate from the water-cooled copper substrate holders and to set the substrate downstream of the plasma. A tungsten grid was used as the anode and the substrate was placed under the grid out of the discharge area. Alternatively, a thick-wall molybdenum tube can also be used as the anode and the substrate was placed on the insulator inside the tube. Hydrogen was flown at a pressure of 50 - 150 Torr and mixed with 0.3 % to 3 % CH₄ flowing at 500 sccm. Either molybdenum or silicon substrate was placed on the silica substrate holder. The ordinary pre-treatment method, scratching with 1 μm diamond powder, was used to prepare the substrate surface. The samples were set at distances of 0, 1, 2, 3 and 5 mm downstream from the anode grid or from the edge of the visible glow discharge area. The deposition time was 5 h at a current density of 1 A cm⁻² and a voltage of 660 V. The results showed that the diamond film growth rate was about 10 μm/h. The structure of the diamond films was analyzed by scanning electron microscopy (SEM), cathodoluminescence spectroscopy (CL), Raman spectroscopy and X-ray diffractometry (XRD). Raman spectra show a diamond line at 1332 cm⁻¹ while XRD diffraction patterns are shown in **Figure 1**.

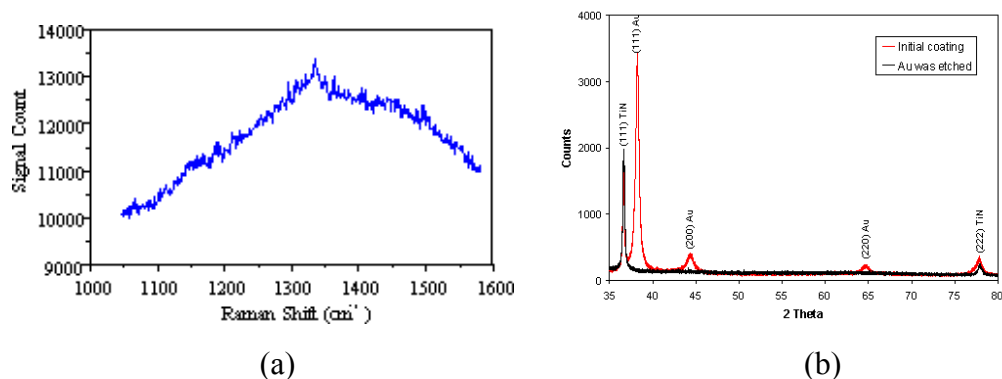


Figure 1 (a) Raman spectra of diamond line at 1332 cm⁻¹, (b) XRD spectra of Diamond film.

Sources: (a) <http://www.chm.bris.ac.uk/pt/diamond/stuthesis/appenda>

(b) <http://www.google.co.th/search?q=xrd+spectra+of+diamond+film&hl=th&lr=&start=10&sa=N>

At 5 mm between the anode grid and the substrate, non-diamond carbon was deposited. X-ray diffraction showed that a well-defined texture of diamond film was grown under the grid while the sample on the insulator inside the tube was mostly polycrystalline. The luminescence band of both samples was similar and observed between 440 - 460 nm and by the colour CL-SEM technique. The homogeneous micro-crystalline structure is shown in **Figure 2**. The diamond crystals emitted light in the blue region, but the wavelength was dependent on the grain sizes of the crystals.

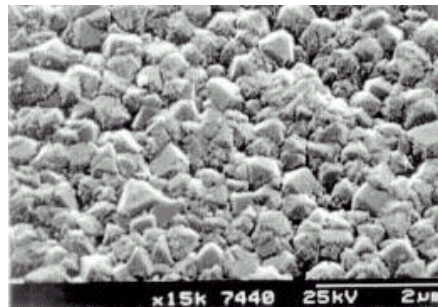


Figure 2 SEM image of diamond crystal.

Source: <http://www.chm.bris.ac.uk/pt/diamond/stuthesis/appenda.htm>

Diamond film deposition using the d.c. glow discharge technique provided higher growth rate than that using an arc-jet system [2]. D.C. glow discharge reactor design is compared with arc jet reactor for material deposition in **Figure 3**. A stable discharge was maintained by a 15 kW pulse-plasma generator. The CH₄ concentrations were varied from 0.5 % to 7 % and the deposition times were set between 5 and 90 h. The gas pressure was controlled at 200 Torr with a simultaneously increasing discharge current limited to 0.5 A and a voltage of 400 V. The diamond films were deposited on molybdenum substrates. The cathode (substrate) temperature was in the range of 900 - 1000 °C. The diamond film from this experiment achieved the highest average thickness of 305 µm and the center thickness of 440 µm at 2 % CH₄ in H₂. The deposition time was 18.3 h at a voltage of 865 V and a current of 4.4 A. The growth rate was determined as 20 µm/h. The crystal morphology and orientation were measured by SEM and XRD, while diamond film purity was determined by micro-Raman spectroscopy.

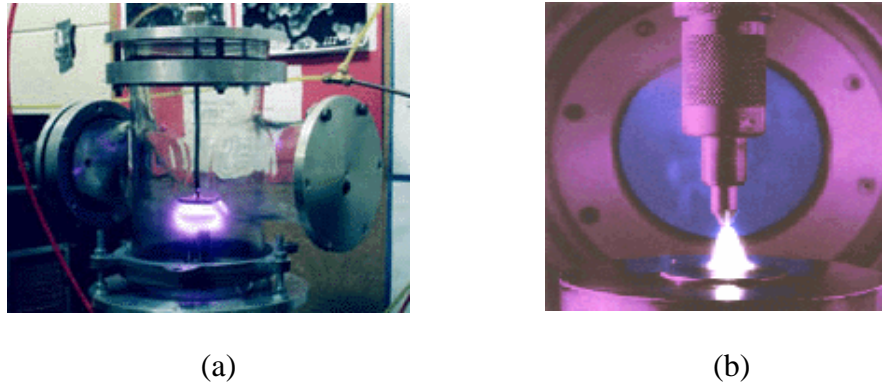


Figure 3 Reactors for material surface deposition

(a) D.C. glow discharge reactor, (b) Arc jet reactor.

Sources: (a) http://www.geocities.com/samir_iliyas/Activity1.html

(b) http://www.me.berkeley.edu/diamond/submissions/diam_review/review.htm

Gu *et al* [3] demonstrated that a diamond film with high thermal conductivity can be prepared by electron-assisted CVD. Two tantalum filaments of 10 mm in length were set 5 mm above a 20 mm × 15 mm silicon substrate placed on a water cooling support. The silicon substrate was polished with 0.5 μm diamond particles. The gas compositions were 0.5 - 5 % CH₄ in H₂ at a pressure of 5.3 kPa (40 Torr). The filament temperature and the substrate temperature were 2000 °C and 700 - 900 °C, respectively. With a 3 A bias current between the filament and the substrate, the growth rate of the diamond film was 3.5 μm/h. The deposition of diamond films was confirmed by Raman spectroscopy, SEM and XRD. The thermal conductivity of the diamond film was measured by the photothermal deflection. The effect of CH₄ concentration at 0.5, 1.0, 2.0, 3.0, 4.0 and 5.0 % CH₄ in H₂ on thermal conductivity of diamond film was analyzed. At lower CH₄ concentration, higher thermal conductivity was obtained because it reduced the impurity of graphitic and non-crystalline carbons in the diamond film. A gas composition of 2 % CH₄ in H₂ was chosen for further experiments. The effect of grain size on the thermal conductivity of the diamond film was studied. The polishing times of the substrate was varied from 3 to 20 min. The longer polishing time showed larger grain size in the diamond film. The change in thermal conductivity depended on the different thicknesses of the diamond film.

The thickness was set from 10 to 160 μm at a fixed substrate polishing time of 15 min. When the thickness of the diamond film was 160 μm , a high thermal conductivity of 8.9 W was obtained.

Yang *et al* [4] studied diamond film growth in an electron-enhanced hot filament CVD system, as seen in **Figure 4**. Normally, low CH_4 concentration and high substrate temperature are desirable conditions. However, lower CH_4 concentration provided lower film growth rates and when the substrate temperature was above 1050 $^\circ\text{C}$, it was hard to form the films. The CH_4/H_2 ratio was varied between 0.5 - 2.5 % of CH_4 in H_2 flowing at 100 ml/min. The substrate temperature was set from 950 to 1250 $^\circ\text{C}$ and the filament temperature was controlled at 2200 $^\circ\text{C}$. After the deposition, Raman spectroscopy and SEM techniques were used to observe the diamond films. They showed a little non-diamond carbon and a large grain size, indicating good conditions for film growth. The Auger emission spectroscopy (AES) and secondary ion mass spectrometry (SIMS) indicated very low impurities of O, Na and N in the diamond film. The heat-resistance of diamond samples was analyzed by thermal gravimetry-differential thermal analysis (TG-DTA). The initial oxidation temperature of natural diamond is at 938 $^\circ\text{C}$. It was concluded that the higher the substrate temperature and the lower the concentration of CH_4 the higher resistivity and oxidation temperature.

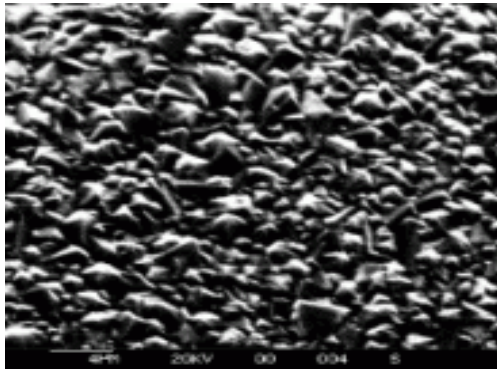


Figure 4 Diamond film growth in an electron-enhanced hot filament CVD system.
Source: <http://www.chm.bris.ac.uk/pt/diamond/semflat.htm>

Diamond film can also be deposited by surface microwave discharges to produce a hemispherical plasma tip [5]. A localized wave launcher containing a field applicator and an impedance matching network was used to excite the surface wave. The plasma density was increased as the plasma reflected at the end of the plasma column. The length of the plasma column was dependent on the microwave power supply. The conditions of the experiment were 0.5 to 1.5 % CH₄ in H₂ gas at a flow rate of 100 sccm with a total pressure ranging from 1 to 60 Torr. The discharge tube was placed in a larger Pyrex tube with a cooling jacket. The surface wave was launched with a waveguide surfatron at 2.45 GHz with power up to 1.8 kW. The substrate temperature was controlled from 500 to 1100 °C and the substrate was placed at a 15 mm distance with respect to the tube. High quality diamond films were obtained at a growth rate of 1.5 μm/h. The films were observed by macro-Raman spectroscopy using an argon laser at 514.5 nm (100 mW). The Raman spectra showed a characteristic peak for diamond at 1332 cm⁻¹.

Jiang *et al* [6] observed the influence of ion bombardment during microwave plasma CVD on the grown film orientation. Polycrystalline diamond films were used as a substrate. It was found that the diamond crystal grew only along the (001) axes of the ion flow direction. The growth conditions selected were as follows: an applied input microwave power of 800 - 1000 W, a substrate temperature was 800 °C, a gas pressure of 25 - 30 mBar (19.5 - 22.5 Torr), an input gas of 0.4 % CH₄ in H₂, a substrate dc bias at -150 V and a growth time of about 20 h. Micro-Raman spectroscopy and SEM were used to investigate the diamond films. The SEM images showed a 10 μm diameter of the films. Raman spectra were shifted from $\nu = 1334 \text{ cm}^{-1}$ to $\nu = 1357 \text{ cm}^{-1}$ for bias-induced films. It was concluded that ion bombardment was effective in improving epitaxial and textural diamond film growth.

The substrate pretreatment is also important for CVD of diamond. Wang and Chen [7] established epitaxial deposition by pyrolysis of silane (SiH₄). The physical fields were separated into three parts.

1) Temperature field: The graphite susceptor was heated by a high frequency generator, then the temperature reduced to that of the water-cooled quartz tube surface.

2) Velocity field: A stagnant layer that existed at the surface of the substrate where the gas did not flow past.

3) Concentration field: In the deposition of silicon film, the gases were H₂ and SiH₄. The silane gas, SiH₄ decomposed to silicon at high temperature and silicon is then deposited on the substrate as a silicon film.

The growth rate of a silicon film was related to the reciprocal temperature. At low substrate temperature, the silicon film was deposited by only a part of the gas in the stagnant layer near the substrate. On the other hand, at high substrate temperature, the silane was completely deposited in the stagnant layer area. Silicon atoms were then rapidly diffused passed the stagnant layer. Thus the rate-controlling process is the rate of atomic silicon diffusion at high temperature but it becomes the rate of SiH_4 decomposition at low temperature. The most suitable temperature for silicon growth is between 900 - 1000 °C. Below 900 °C, the silicon decomposition is polycrystalline. The film shows slow growth rate and low quality, because the SiH_4 decomposes very fast and is blown away by the gas flow.

Recently using methane or other basic hydrocarbon compounds instead of SiH_4 , the growth condition of single-crystal diamond films can be estimated. The formation energy of CH_4 (17.89 kcal/mol) is higher than that of SiH_4 (14.8 kcal/mol), and also the bond energy of C-H bond (414 kJ/mol) is higher than that of Si-H bond (318 kJ/mol). Thus the decomposition temperature of methane should be much higher than that of silane.

From the deposition rate:

$$\begin{aligned} -\Delta H_{\text{CH}_4} / RT &= -\Delta H_{\text{SiH}_4} / RT \\ \Delta H_{\text{CH}_4} / T &= \Delta H_{\text{SiH}_4} / T \end{aligned}$$

$$\text{Substituted as } 17.89 / T = 14.8 / (950+273),$$

(The appropriate temperature for decomposition of SiH_4 is equal to 950 °C)

So a temperature of 1100 °C is suitable for decomposition of CH_4 in diamond thin film deposition. From the bond energy ratio of CH_4 and SiH_4 , the deposition temperature for single-crystal diamond film is estimated to be 1300 °C. Therefore, the range of substrate temperature was set at 1100 - 1300 °C. Thermal deposition of the gas phase and a conventional CVD reactor were used to deposit single-crystalline diamond films at controlled temperatures below 1100 °C. The silicon substrate was scratched, firstly to etch the (100) silicon to arrange tiny holes for putting small diamond particles in as seeds, and let them grow to produce a diamond film. Water-free alcohol, at a temperature between 1100 and 1250 °C, was adopted as the carbon source. Because the bond energy of the C-C bond (347 kJ/mol) is lower than that of the C-O bond (360 kJ/mol), the decomposition temperature of water-free alcohol should be lower than that of CH_4 . The diamond film was grown at atmospheric pressure with a gas flow of 10 - 12 cm/s. The growth rate was 330 Å/h.

The quality and characteristics of the film were observed by Raman spectroscopy and refraction electron diffraction techniques.

Fuchs *et al* [8] studied the surface modification on silicon (100) substrates for CVD diamond deposition. The diamond film was produced with low porosity, low mechanical stress and high adhesion on the substrate. The nucleation process initially occurred at a mechanically polished silicon surface. The nucleation density was found to be up to 10^{10} atoms/cm² exposed by a negatively biased silicon substrate of the mixed gas, 5 - 40 % CH₄ in H₂. The effect on the substrate surface was studied by atomic force microscopy (AFM). The substrate was cut into 10 mm × 20 mm in planes and cleaned with ethanol and acetone. A tantalum filament was heated under a H₂ atmosphere in a hot-filament reactor until the substrate temperature reached 600 - 700 °C. The reaction time was 5 - 20 min. The mixed gases were hydrogen flowing at 0 - 400 sccm, CH₄ flowing at 0-10 sccm and Ar flowing at 136 sccm. AFM images such as that shown in **Figure 5** reveal that the surface of an untreated (100) silicon wafer was very flat surface with an rms-roughness of less than 0.1 nm. However, the rms-roughness increased to 0.3 nm for the substrate surface after 5 min of bias conditions and to 1.1 nm under 2.5 % CH₄ in a H₂ atmosphere for 20 min. However, under a pure H₂ atmosphere, the surface roughness was increased to 2.1 nm. It was concluded that the longer reaction time, the higher substrate roughness that was obtained.

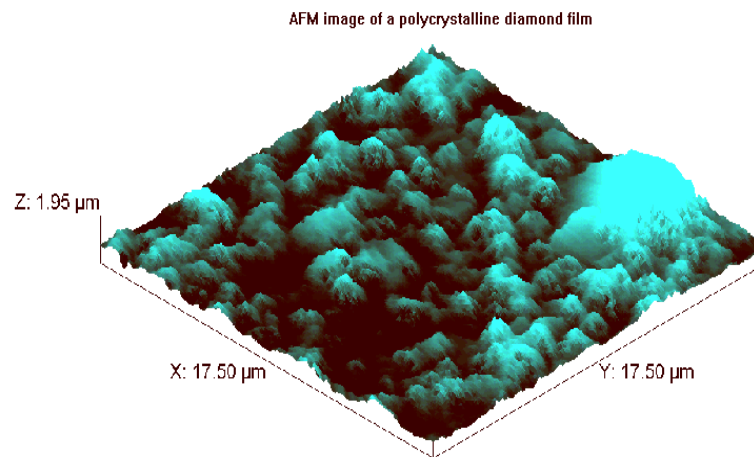


Figure 5 AFM image of diamond crystal.

Source: <http://www.chm.bris.ac.uk/pt/diamond/semflat.htm>

Two competitive reactions on thermodynamic simulations were calculated with the Equicalc software, their reactions were follows:



In the first reaction, the removal of a natural oxide occurred. In the second, possible etching occurred by hydride formation. Carbide formation (CH_4/H_2 mixture) was shown to occur as follows:



In this case the etching effect should be less pronounced, because of the lower sensitivity of silicon carbide to hydrogen etching.

CONCLUSIONS

With the rapid progress in diamond film deposition technology, it should not be too long before this advanced technology begins to make a significant impact in many areas of modern life. However, several issues need to be addressed. Growth rates should be increased (by one or more orders of magnitude) without loss of film quality. Deposition temperature should be reduced, for substrates with low melting points. This also increases the number of substrates onto which adherent diamond films can be deposited. A better understanding of the nucleation process is required, hopefully leading to an elimination of the poorly controlled pre-abrasion step. Substrate areas should also be scaled up, without loss of uniformity or film quality. At present, there is a huge amount of work being done throughout the world on solving these issues and progress is being made seemingly on a daily basis. If this continues, the future of growing single-crystalline diamond film looks bright indeed.

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บทคัดย่อ

สรารุช เดชมณี

หลักพื้นฐานของการปลูกฟิล์มเพชรแบบผลึกเดี่ยว

บทความนี้กล่าวถึงการปลูกฟิล์มเพชรแบบผลึกเดี่ยว โดยใช้วิธีไอสารเคมีแบบต่างๆ นอกจากนี้ได้เปรียบเทียบเงื่อนไขตัวแปรในการปลูก เช่น วัสดุรองรับ ส่วนผสมของก๊าซ อุณหภูมิ ความดัน ที่ทำให้ได้ฟิล์มที่เหมาะสมที่สุด ประเด็นสุดท้ายที่กล่าวถึง คือ เทคนิคการวิเคราะห์ฟิล์มเพชร เช่น รามานสเปกโทรสโกปี จุลทรรศน์อิเล็กตรอนแบบส่องกราดและการเลี้ยวเบนของเอ็กซ์เรย์