



Thermodynamic stability of graphitic diamond films produced using CCVD apparatus

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Synopsis

Diamond synthesis has attracted a great deal of interest because of its exceptional properties and various applications. In this study, the chemical catalytic vapour deposition (CCVD) method was used to synthesize diamond films using acetylene as carbon source and hydrogen as carrier gas at a temperature of 1000°C, and their thermodynamic stability was studied. Photographic analysis revealed that these products are diamond films, Raman spectroscopy confirmed that they are graphitic while confocal laser scanning microscopic image analyses proved that these diamonds films have structural defects due to iron impurity from the catalyst precursor. The quantity of diamonds films produced is also proportional to the acetylene to hydrogen ratio but these films are larger in size at lower acetylene to hydrogen ratio. Thermogravimetric analyses showed that transformation of these materials begins at 25°C but could not be used to determine if a temperature range below 25°C exists. The stability of these CCVD-synthesized diamonds also increases below 25°C when stored at different temperatures.

Introduction

Probably more than any other gemstone, diamonds feature more predominantly in the history and cultural heritage of the human race¹. The stable crystalline phase of carbon is graphite, but it can be transformed into its most remarkable phase for applications: diamonds². The scarcity of diamonds has resulted in their appreciation for thousands of years. The unique optical properties of diamond were utilized through the polishing techniques developed in the late fifteenth century. The mining, polishing, trading and retailing of these gems have led to the development of worldwide industries in the more recent centuries. The aesthetically pleasing diamond is integrated into jewellery and a variety of other applications³.

Natural diamonds are produced within the Earth's mantle by a high-pressure and high-temperature phase conversion of graphite. Volcanic action then results in the transportation of the diamond into the Earth's crust. During the late 18th century with the study of chemistry, the composition of

diamond was established. In 1796, Smithson Tennant studied the combustion of diamond and showed that it has the same composition as other forms of carbon⁴.

Many attempts have been made to synthesize diamond artificially using another commonly occurring form of carbon, graphite as a starting material. This proved extremely difficult, mainly because at room temperature and pressure, graphite is the thermodynamically stable allotrope of carbon. Although the standard enthalpies of diamond and graphite differ only by 2.9 kJ mol⁻¹⁵, a large activation barrier separates the two phases preventing interconversion between them at room temperature and pressure. Ironically, this large energy barrier, which makes diamond so rare, is also responsible for its existence, since diamond, once formed, cannot spontaneously convert to the more stable graphite phase. Thus, diamond is said to be metastable, that is, kinetically stable but not thermodynamically stable. To overcome these problems, researchers realized that conditions are needed where diamond is the more stable phase. There is no easy rearrangement mechanism by which diamond can convert to graphite.

The knowledge of the conditions under which natural diamond is formed deep underground suggested that diamond could be formed by heating carbon under extreme pressure. This process forms the basis of the so-called high-pressure high-temperature (HPHT) growth technique⁶, first marketed by General Electric, which has been used to produce 'industrial diamond' for several decades. In this process, graphite is compressed in a hydraulic press to tens of thousands of atmospheres, heated to over

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2 000 K in the presence of a suitable metal catalyst, and left until diamond crystallizes. However, the drawback of the HPHT method is that it still produces diamond in the form of single crystals ranging in size from nanometres to millimetres, and this limits the range of applications for which it can be used. However, with the recent development of techniques for depositing thin films of diamond on a variety of substrate materials, it is now possible to exploit these superlative properties in many new and exciting applications.

The objective of this work is to establish the thermodynamic stability of synthetic diamond produced by CVD in order to establish the dependence of the diamond stability on structure, and determine a relative thermodynamic stability of the allotropic modifications of carbon.

Experimental

The synthesis of diamond films was performed in a swirled floating catalyst chemical vapour deposition reactor (SFCCVD), which has been previously described⁷⁻⁸. Briefly, it consists of a vertical quartz reactor loaded in a tubular furnace. Gases (argon, nitrogen, hydrogen and acetylene) flow into the reactor with the aid of system of valves and rotameters through a swirled coiled passage, which leads from catalyst vaporizer. Nitrogen gas is passed through the system, while keeping all the other valves closed in order to flush out contaminants and to ensure that there are no leakages. Argon is then passed through the apparatus to prevent unwanted reactions from occurring. The mantle, which heats the catalyst vaporizer, and the furnace are set to the desired temperatures. A specified quantity of ferrocene, which is dissolved in xylene, is pumped into the vaporizer periodically. The catalyst is evaporated and transported into the reactor by acetylene and hydrogen gases. The smoky products or carbon vapour evolved from the upper end of the reactor are cooled at the condenser and collected in the two cyclones.

Results and discussion

Photographic images

The photographic images of diamonds films produced using

CVD apparatus at 1 000°C and different acetylene to hydrogen flow ratios are presented in Figure 1. Many colours visible in the figure indicate that spectral diffraction has occurred. Based on the refractive index and dispersion of light in diamond, this supports the presumption that these particles are diamond films.

Confocal microscopy

Figure 2a and b indicate that laser reflection on the sample shows ultrafluorescence in red and green lights. Pure diamonds do not fluoresce under visible light, but only under X-ray light. This indicates that the diamonds have defects or impurities. The impurities in the diamonds are possibly ferrous in nature, which was from the ferrocene catalyst. These impurities may negatively affect the stability of the graphitic diamond films. Consequently, this is indicative of the requirement to remove the impurities in order to improve the thermodynamic stability. From the 2D image (Figure 2c), which was obtained using transmitted light without laser light, the fluorescent areas in Figure 2a and Figure 2b correspond with an area in the image of the sample that appears to contain impurities. Figure 2d is the 3D image obtained by optical sectioning with images 0.5 microns apart. The images were then stacked to create an image. This image shows the surface of the diamond film with improved clarity and detail.

Stable conditions

The first sample containing the diamond films was stored at an elevated temperature of 90°C. The diamond films rapidly transformed within ten minutes, an indication that the diamond films are thermodynamically unstable at a temperature of 90°C. The storage temperature was varied in order to determine the temperature at which the sample would remain stable. The results are presented in Table I.

Since the conversion time is dependent on numerous factors such as the quantity of diamond in the sample and the humidity, three samples were allowed to transform at ambient conditions of approximately 25°C. It was established that the diamond films were converted to graphite in approximately two weeks at ambient conditions. The conversion period of the refrigerated sample (about 7°C) showed stability

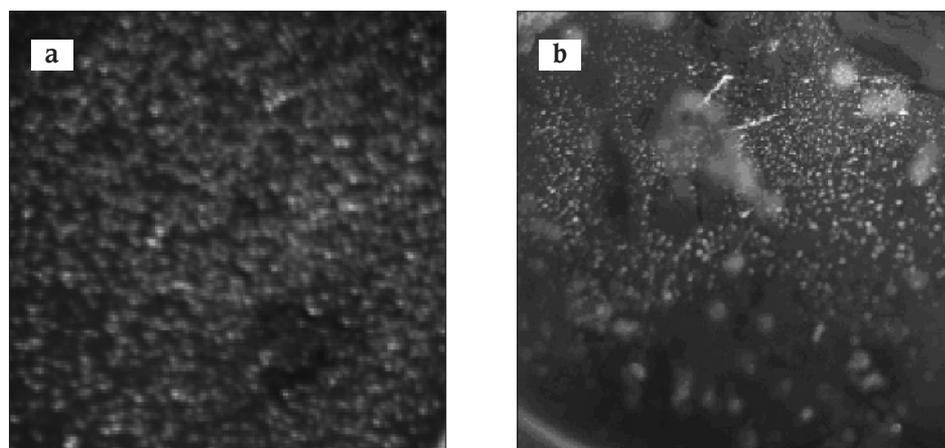


Figure 1—Photographic images of diamond produced at acetylene to hydrogen ratio of (a) 3: 1 and (b) 3: 2

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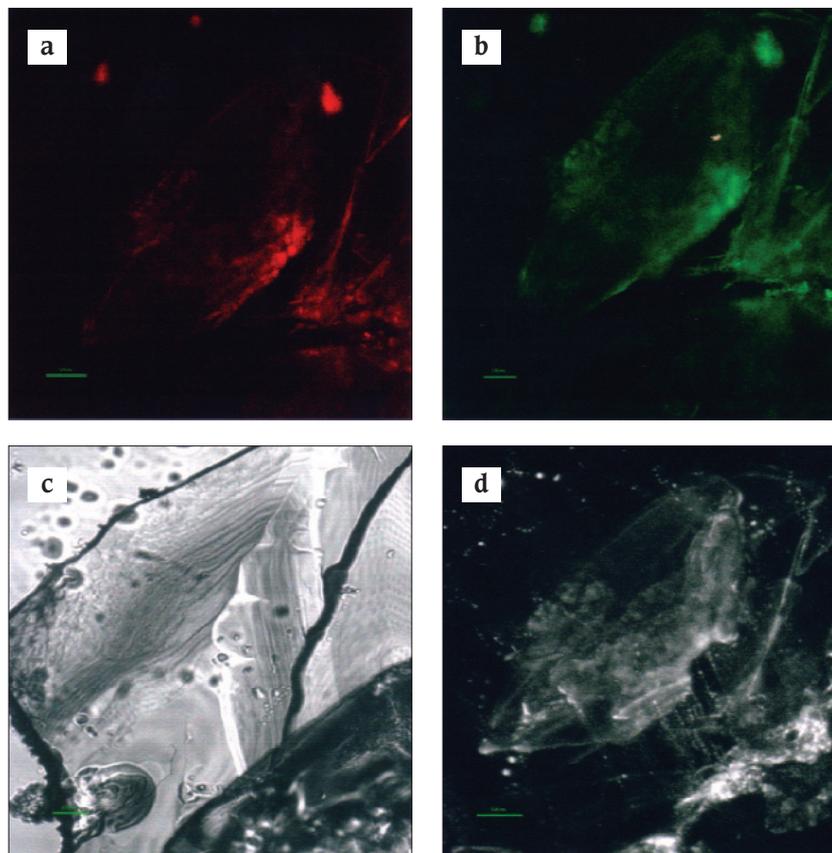


Figure 2—Images obtained from the Confocal Laser Scanning Microscope in (a) fluorescent red light (b) fluorescent green light (c) 2D image from transmitted light (d) 3D image from optical sectioning

Storage temperature (°C)	Time to decompose
90	< 10 Minutes
±25	± 2 Weeks
7.1	> 2.5 Weeks

for about two and a half weeks. It can therefore be established that these materials are thermodynamically unstable between 25 and 90°C and stable at 7.1°C (Table I). In other words, lower temperature favours the stability of the diamond films.

Thermogravimetric analysis (TGA)

TGA was used to measure the changes in the mass of diamonds sample as a function of temperature. The sample consisted of some black graphitic materials, the nature of which was not determined, and some diamond films. A horizontal line would indicate a constant mass for the corresponding temperature range; it would therefore indicate that the diamonds remain stable within the temperature range and would be the desirable result. Figure 3 shows weight loss of the sample as a function of temperature. The mass of the sample decreases at an approximate temperature of 25°C because the diamond films decompose early during

the analysis. The curve levels out at approximately 350°C as all the diamond films have decomposed, and the volatiles have been boiled off. The remainder of the graphitic material has constant mass (is stable) until approximately 530°C, at which temperature it begins to lose mass.

The results are in agreement with the observations made at the stored conditions described earlier. These results also disprove the hypothesis that the diamond films are stable at 25°C and 1 atm. From a thermodynamic point of view, the conversion of graphite into diamond is characterized by a small, positive value of ΔG° at 25°C and 1 atm pressure as shown in Equation [1]:

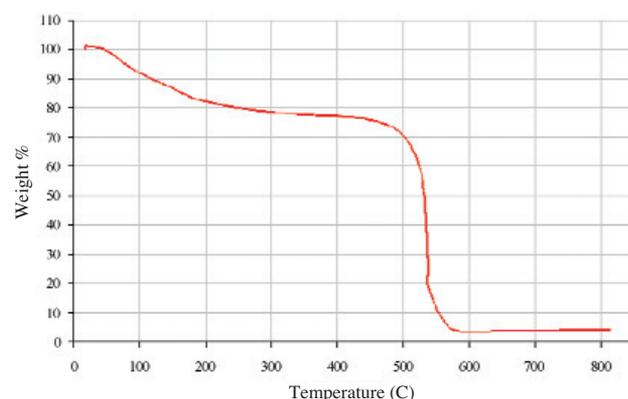


Figure 3—TGA diamond data analysis

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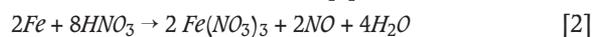
This indicates that diamond is thermodynamically unstable with respect to graphite at these conditions and that the reaction has thermodynamic permission to proceed in the opposite direction. Unfortunately, the thermodynamics does not give any information about the time required for a reaction to take place, and the diamond to graphite conversion is extremely slow under ordinary conditions. Increasing the temperature enables the acceleration of most reactions and this is also true for the conversion of diamond to graphite.

Raman spectroscopy

The Raman spectroscopy of the diamond sample is shown in Figure 4. It is known that pure diamond produces a single sharp peak at 1332 cm^{-1} but a shifted single sharp peak at 1381.4 cm^{-1} was obtained in this figure, which is expected because CVD diamond has a shifted peak. This shifted peak may be due to defects, surface structures, amorphous material, diamond transformation to graphite or any impurities in the sample.

Purification process

purification method was explored to verify the stability of the graphitic diamond film since the removal of the ferrous impurities should increase the stability of the sample. The removal of the impurities by the reaction with nitric acid was explored⁹⁻¹² as shown in Equation [2].



This method could not purify the diamond samples as they all disappeared in the acid. The reaction mechanism of this disappearance could be explained from enthalpy of the reaction. From Hess's law and tables of standard enthalpies of formation, the reaction enthalpy was calculated to be 980.015 kJ.mol^{-1} . This value indicates that heat was released during the exothermic reaction between iron and nitric acid. Since the diamond films are thermodynamically unstable and the transformation accelerates at elevated temperatures, the conversion to graphite would occur due to the addition of heat from the reaction.

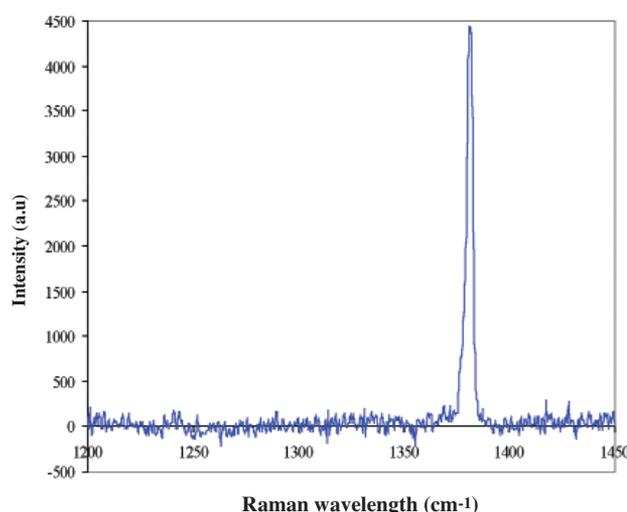


Figure 4—Raman spectrum of apparent diamond film sample

Conclusion

Apparent diamond films were produced using CVD apparatus at a temperature of 1 000 °C. Since a carbon source was used as a precursor, it is conclusive that the samples produced were made of the carbon element. The Raman spectrum obtained shows a single, sharp diamond peak at 1381.4 cm^{-1} . These characteristics combined indicate that the material obtained is most likely to be graphitic diamond. The TGA results and the observations made at the conditions at which the samples were stored disprove the hypothesis that the diamonds are stable at 25 °C and 1 atm. Because the molar entropy of graphite is greater than that of diamond, the thermodynamic instability of diamond increases with increasing temperature. For this reason, greater pressures are necessary to bring graphite and diamond into equilibrium with each another with increasing temperature. The quantity of diamonds produced appears to be proportional to the acetylene to hydrogen ratio. The apparent proportional relationship between the acetylene and hydrogen ratio and the quantity of diamonds produced holds only while there is a sufficient quantity of acetylene. The diamond films produced at a lower acetylene to hydrogen ratio appeared larger in size. This observation confirms that in order to make a smaller size diamond grain, it is necessary to increase the ratio of carbon to hydrogen.

References

1. WARD, F. *Diamonds*. Bethesda, MD: Gem. 1998.
2. RATY, J. and GALLI, G. Nanodiamonds. *Encyclopedia of Nanoscience and Nanotechnology*. Marcel Dekker, Inc., California, U.S.A. 2004.
3. <http://www.chm.bris.ac.uk/pt/diamond/mattthesis/chapter1.htm> (last updated: 06/06/06).
4. TENNANT, S. *Phil. Trans. R. Soc. Lond.*, 1797. vol. 87. p. 123.
5. BUNDY, F.P. *J. Geophys. Res.*, 1980. vol. 85. p. 6930.
6. <http://www.zeis.com> (cited: 28/10/06)
7. IYUKE, S.E. Swirled Fluidised Bed Chemical Vapour Deposition Reactor. SA Patent Application no.: 2005/03438. 2005.
8. IYUKE, S.E., PIENAAR, C., ABDULKAREEM, S.A., and AFOLABI, A.S. SAICHE Conf. Proc. Durban. 2006.
9. WANG, W., Woo, K.-D., and KIM, D.-K. *Energy Conversion and Management* 47, 2006. pp. 3235–3240.
10. MONTORO, L.A. and ROSOLEN, J.M. Carbon. Article in press. 2006.
11. ZHANG, F., SHEN, J., SUN, J., ZHU, Y. Q., WANG, G., and MCCARTNEY, G. *Carbon* pp. 1254–1258.
12. Conteau, E., Hernadi, K., Seo, K., Seo, J.W., Thien – Nga, L., Miko, Cs., Gaal, R., and Forro, L. 2003, *Journal of Chemical Physics Letter*, vol. 378. pp. 9–17. ◆