DIAMOND NUCLEATION ON GRAPHITE SUBSTRATE USING A PURE HYDROGEN FEED

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Diamond particles and films were grown on graphite substrates using hot-filament CVD method with a pure hydrogen feed. After deposition, graphite substrates showed strong etching effects. A trough of 1 mm deep and 4-5 mm wide was formed in the graphite opposite to the filament. Scanning electron microscopy and micro-Raman spectrum demonstrate that diamond has grown both inside and near the edge of the trough. The results are discussed with respect to the possible precursors of diamond deposition and the effect of atomic hydrogen interaction with graphite substrates.

INTRODUCTION

Among the techniques for diamond synthesis at low pressure[1-4], hot-filament chemical vapor deposition (HFCVD) is a very promising process due to its simplicity. The HFCVD method, requires only a filament and a current source to decompose the hydrocarbon species (typically CH_4) into methyl radicals and hydrogen molecules into atomic hydrogen. At a filament temperature between 2000°C to 2200°C and gas pressure of 30 to 80 torr, diamond particles or films can be deposited onto a heated substrate at 700°C - 1000°C. It has been shown that[5]: (a) the techniques for activation (microwave, hot-filament, plasma arc, or combustion), or (b) the hydrocarbon species (CH_4, C_2H_2, CO_2, etc.) are not major factors for the growth of diamond. In contrast to the well-established techniques of CVD diamond deposition, the detailed growth mechanisms of diamond are still not well understood. It is generally believed that atomic hydrogen is important in both diamond nucleation and growth[6]. The enhanced etching rate of graphite by atomic hydrogen plays a major role in preventing the growth of graphite, and in promoting diamond formation in this non-equilibrium process. The chemical erosion of graphite by hydrogen impact has been studied[7] in the context of potential use of graphite as an inner wall liner in thermal nuclear reactors. For example, Balooch and Olander[8] have shown that at temperatures less than 1000°K the main reaction product was methane (CH_4), and at temperatures > 1100°K, the major erosion product was acetylene, (C_2H_2). Vietzke et al[9] find evidence that the reaction product was actually CH_3^* rather than CH_4.

In view of the fact that CH_4, C_2H_2, and CH_3^* have all been proposed as precursors for the CVD diamond film growth, it would be intriguing to find out whether the products from the hydrogen-carbon interaction *alone* can be used as precursors for diamond thin film growth in a pure hydrogen environment. In the following we report the deposition of diamond thin films and particles on graphite substrates with a pure hydrogen feed. This demonstrates that the chemical reaction products in the hydrogen-graphite reaction can be used as an efficient starting material for diamond growth.

EXPERIMENTAL

The HFCVD technique was employed with a straight vertical tungsten filament from Johnson Matthey, 5cm in length and 0.75mm in diameter was used. The distance between the filament and the substrate was kept at 2-3 mm using a micro-positioner. High purity hydrogen (99.999%) was used with a flow rate between 10-20 sccm. We notice that this flow rate is about a factor of ten less than the typical CH_4/H_2 flow rates used in conventional CVD diamond growth. This slower flow rate is necessary to prevent the rapid removal of hydrogen-carbon reaction products. The pressure of the deposition chamber, as measured by a manometer and regulated by valves, was maintained at 40 Torr through out the experiment. The HFCVD chamber is made of stainless steel and is water-cooled on the outside. A mechanical pump is used for evacuation of the chamber. Before deposition, the tungsten filament is pre-carburized[10] in 1.2% methane/hydrogen mixture for one hour at approx. 1950°C. After pre-carburization, the chamber was re-evacuated before admitting the pure hydrogen gas. During deposition, current through the filament was kept at 65 A. The temperature of the filament was determined by a pyrometer to be about 2000°C, and the substrate temperature directly

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in front of the W filament was measured by a thermocouple to be about 900°C. The substrate used is a 99.5% purity graphite sheet from Johnson Matthey. Typical deposition times were between 5-20 hours.

RESULTS

In Figure 1, the general feature of a graphite substrate after 17 hours deposition is shown. Here we can see that in the HFCVD process the hydrogen erosion of graphite is quite substantial. The portion near the filament shows a hemi-cylindrical trough with a depth of 1-2 mm. From that we estimated the etching rate in front of the W filament is about 1-2 micron/min. The graphite substrate after deposition was examined under scanning electron microscope(SEM). Two different morphologies were observed. In one type, diamond micro-crystalline particles formed a crust and covered the surface near the trough. The other type is individual particles near the bottom of the trough.

In Figure 2, three SEM micrographs are presented. In the first a crust of diamond aggregate is observed near the edge of trough. Triangular (111) facets of individual diamond particles are clearly visible. This finding agrees with previous results[11] that the diamond morphology is dominated by (111) faces when the concentration of CH_4 is less than 0.4%. The micrograph in Fig. 2b, shows individual diamond particles at the bottom of the trough. The most intriguing result is the observation of a rectangular shaped single crystalline diamond plate(Fig. 2c). The micro-Raman spectrum[12] of this diamond plate exhibits a narrow peak at 1333 cm^{-1} which is indicative of the diamond structure. The broad band centered at 1580 cm^{-1} indicates graphitic contamination.

DISCUSSION

Graphite has seldom been used as a substrate for diamond deposition in the past. The general consensus is that the graphite surface tends to promote sp^2 (graphitic) bonding rather the sp^3 (diamond) bonding. In addition, the graphite substrate in the CVD chamber tends to act as a

carbon source and may change the hydrocarbon/hydrogen ratio. More recently, several groups have studied the CVD diamond growth on graphite substrates and showed that graphite intermediates can act as nucleation sites for diamond. For example, Z. Li et al[13], Ong, Xiong, Chang and White[14], and Dubray, Pantano and Yarbrough[15] have studied the CVD growth of diamond on highly oriented pyrolytic graphite (HOPG) crystals. They all found that diamond crystals were mainly nucleated at the prism plane, rather than at the basal plane of the graphite sheet. Z. Li et al[13] and W. Lambrecht et al[16] further proposed that there was a preferential epitaxial relationship between graphite and diamond.

Figure 2.   SEM micrographs of the same sample shown above.   (a) Diamond particles aggregate at the surface, showing (111) faces, (b) diamond particles inside the trough shown as white spots, (c) a large plate-like single crystalline diamond.
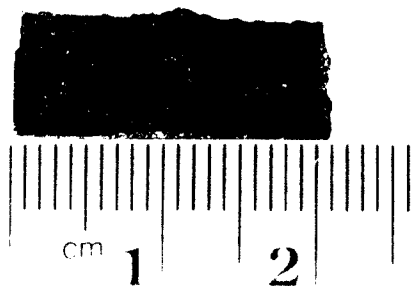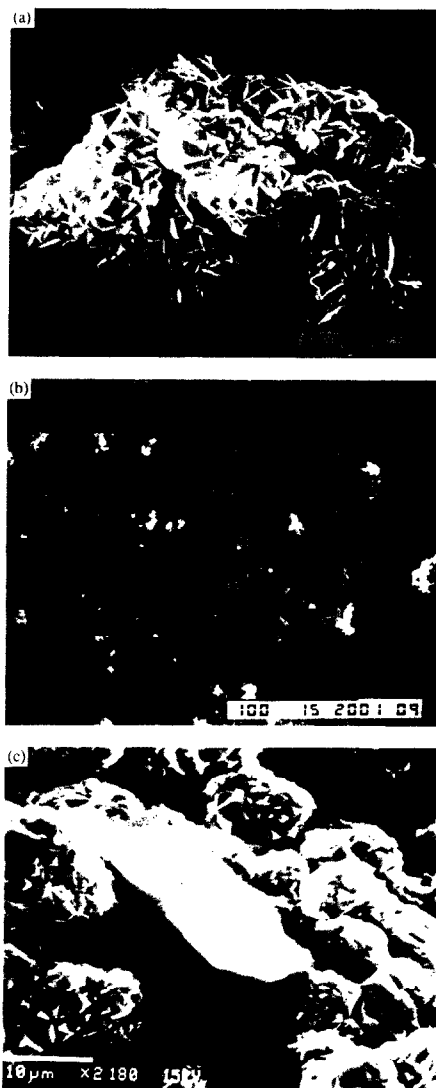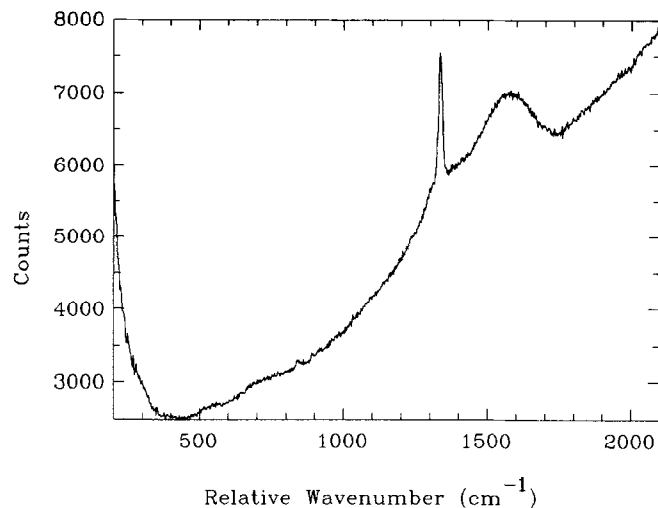

Figure 1.   A global picture of the graphite substrate after 17 hrs CVD diamond growth.   A trough 4 mm wide and 1 mm deep was formed near the center of the graphite substrate.

Figure 3. Micro-Raman spectrum of diamond plate shown in Fig.2(c). The excitation used is the 514nm line of an Ar ion laser.

The initial nucleation site of diamond has been actively debated in the past. In addition to the graphite intermediates mentioned above, other mechanisms of nucleation have been suggested. For example, nano-size diamond particles[17] left on the scratched substrates, the surface damages created by scratch or ion beam bombardment[18], and carbide[19] formed on the substrates have all been proposed as the initial nucleation sites for diamond growth. However, our observation of the large plate-like diamond particle in Fig. 2(c) is difficult to reconcile with any of the above models. The observed shape seems to imply that diamond has grown epitaxially on a flat surface. This may be due to direct conversion of a particular graphite surface to diamond as proposed by Z. Li et al[13] under intense atomic hydrogen bombardment.

In summary, we have achieved the deposition of diamond films and particles on graphite substrate in a pure hydrogen environment without any external carbon containing gases. This result is supported by the fact that hydrogen-carbon interaction is rather strong[20]. The reaction products of the hydrogen-carbon interaction, (like CH_4, CH^*_3, or C_2H_2) presented near the vicinity of the substrate, appear to be responsible for the precursors of diamond growth.

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