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Mechanism of graphitization and optical degradation of CVD diamond films by rapid heating treatment

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ABSTRACT

Polycrystalline CVD free-standing diamond films have been heat treated through a rapid heating process using a direct current (DC) arc plasma jet system within the temperature range of 1500–2000 °C. The optical transmission of the diamond film decreases when the treatment temperature exceeds 1500 °C. When the diamond film was annealed to 1800 °C for just 1 min, the infrared (IR) transmittance at $\lambda = 10.6$ μm of the film was significantly decreased from 60.5% to 4.0%, due to the transformation from diamond to graphite. Further increase of the temperature to 2000 °C leads to complete loss of optical transmittance in only 30 s, due to the detrimental occurrence of graphitization. XRD patterns indicate that graphite ultimately grows preferentially along the (0002) plane by forming disordered or turbostratic graphite as intermediate product. Raman spectra and SEM images verify that at 1500–1850 °C graphitic carbon transforms from the diamond surface in the form of protruding submicron crystallites, which were still containing a number of sp^3 C—C bonds. In addition to graphitization on the external surface, the diamond-graphite phase transition also occurs along the grain boundaries and the calculated activation energy of the grain boundary graphitization process is 276 $kJ \cdot mol^{-1}$ for the CVD diamond.

1. Introduction

Diamond is a favorable transparent material with a wave range from ultraviolet to far IR (225 nm–25 μm) except from the absorption peaks within the 3–6 μm range due to the phonon oscillation [1]. The theoretical transmittance of high quality diamond is 71.4% [2] in the far IR region (8–12 μm). In addition to optical advantages, the outstanding thermal and mechanical properties of diamond make it an excellent material for potential use in manufacturing far IR windows for severe application conditions [3]. The appearance of large area planar and dome-shaped self-standing diamond films fabricated by the chemical vapor deposition (CVD) method makes the application come true. However, CVD diamond far IR windows will be heated to an ultra-high temperature instantly through aerodynamic heating when they are applied in hypersonic flight vehicles. If flying speed is higher than 6 Mach, it is inevitable that the stagnation temperature exceeds 1500 °C [4] and the ambient gas may be ionized. Temperature induced diamond to graphite phase transitions will occur and the effect on IR transmittance of CVD diamond films is critical for such extreme applications. The purpose of this article is to investigate the graphitization behavior and the optical degradation of polycrystalline CVD self-standing diamond films after elevated temperatures rapid heating treatment.

In 1924, Friedel and Ribaud [5] first published that graphite layers formed on the octahedral-shaped natural diamond surface during heating in vacuum at the temperature range 1500–1800 °C and diamond completely transformed to graphite at 1900 °C. Annealing at 1400 °C, by contrast, resulted in the graphitization of the implanted damaged sub-surface layer rather than the whole diamond [6]. Evans and James [7] reported that very slight graphitization can be detected in a single crystal diamond after heating at 1500 °C under high vacuum or non-oxidizing conditions. By calculating the temperature dependent graphitization rate, they also obtained the activation energy for the surface graphitization process, which is 1060 $kJ \cdot mol^{-1}$ for the (111) surface, and 730 $kJ \cdot mol^{-1}$ for the (110) surface. Graphitization of diamond is also strongly dependent on diamond shape. Graphitization of nano-diamonds has also attracted the interest of a considerable amount of researches, focused on either experimental or simulation studies [8,9]. The reason why the onset temperature for graphitization of nano-particle is lower than that of bulk diamond is the decrease in activation energy, caused by the large surface-to-volume ratio of nano-diamond [10].

Graphitization and optical properties of polycrystalline CVD diamond films after high temperature treatment have also been studied in details [11,12]. The formation of the graphite-like phase results in a progressive darkening and the enhancement of optical absorption at temperatures higher than 1300 °C. Volume expansion was observed with 85% graphite phase and 15% diamond phase at temperature up to 1700 °C. Further research revealed that graphitization at grain

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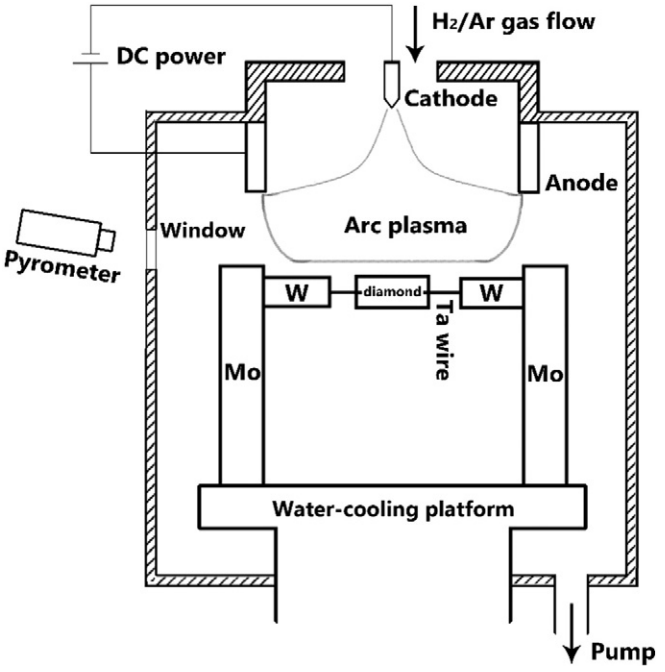

Fig. 1. Schematic diagram of the rapid heating treatment device. The DC arc plasma jet system includes a vacuum chamber, DC power source, cathode/anode, water-cooling platform and pumping system. The additional device (Mo, W and Ta wire) was used to suspend the diamond sample. The IR pyrometer is in fact perpendicular to the paper plane and it aims at the sample.

boundaries even enhanced the fracture strength of CVD diamond [13]. Furthermore, it should be clarified that this transformation is not an equilibrium phase transition so that isothermal process at transformation point will not occur.

Usually, annealing might consume a lot of time during heating up towards the target temperatures. Thus, two stages, including a heating up stage and an isothermal treatment stage, were investigated in combination for such a non-equilibrium phase transition. Consequently, it is necessary to investigate the effect of instantaneous heating treatment on polycrystalline CVD diamond films in order to guide applications for supersonic vehicles. Ultrafast heating rate and short holding time has been proved to be an effective way to prevent graphitization of diamond in sintering diamond composites [14]. Heat treatment through the rapid heating process by direct current arc plasma jet system has been lately used for annealing CVD diamonds [15,16], greatly decreasing the residence time in sub-high temperature of diamonds. In their previous work, the most important finding is that significant enhancement of fracture strength was observed in the diamond films with neither obvious graphitization nor weight loss, even though the annealing temperatures were among 1500–1800 °C, which were considered as graphitization occurrence temperature range. However, they did not study any optical properties of the diamond films. In the present work, optical grade polycrystalline CVD self-standing diamond films were successfully treated at high temperatures (1500–2000 °C) by arc plasma rapid heating process and the graphitization behavior was studied along with the IR properties.

2. Experimental

Diamond film specimens of $L \times W = 10 \times 5\ mm^2$ were laser cut from a Φ100 mm free-standing diamond wafer, which was polished in both sides. The initial polycrystalline diamond wafer was deposited on Mo substrate at 1000–1100 °C with gas mixture of $H_2/Ar/CH_4$ by a high power DC arc plasma jet CVD device as described elsewhere [17]. After deposition process, the diamond wafer separated from the substrate when the temperature returned to room temperature due to the different thermal expansivity between diamond and molybdenum. The average thickness was approximately 1.7 mm after growth and 870 ± 10 μm after polishing. After laser cutting, the samples were cleaned in boiling $H_2SO_4 + HNO_3$ (the volume ratio is 5:1) solution to remove any adhering graphite and then rinsed by deionized water. The roughness of diamond films was lower than 15 nm and the IR transmittance ($\lambda = 10.6\ \mu m$) was 60% (±2%).

Diamond specimens were heat treated at 1500 °C, 1600 °C, 1700 °C, 1800 °C, 1850 °C, 1900 °C and 2000 °C for 30 s, 60 s and 90 s in DC arc plasma by the same equipment as the diamond growth process. The heat source was generated by an electric breakdown of H_2/Ar flow at high voltage. In order to reduce heat conducting area and isolate water-cooling platform, an additional device, including two molybdenum stanchions, tungsten bars and tantalum wires, was used to suspend the diamond films (Fig. 1). Moreover, on each diamond specimen two milli-pores were perforated on the edges of both sides in order for a tantalum filament to be able to fix it in place. As a result, diamond films can be rapidly heated to high temperatures. The heated samples were rapidly cooled in argon flow after power was off. The treating temperatures were measured by an IR pyrometer. Since the IR emission coefficient of samples might change under high temperatures due to diamond-graphite phase transitions, different target temperatures with different parameters were calibrated by using a graphite slice as standard specimen. The heat treatment parameters are listed in Table 1.

Optical transmittance measurements were carried out using an Excalibur HE 3100 FTIR spectrometer at room temperature. The X-ray diffraction (XRD) patterns were obtained on a Smartlab diffractometer using Cu K_α radiation. Raman mapping and micro-Raman spectra were obtained by a Nanophoton Raman-11 microscope with a laser wavelength of 532 nm and a LabRAM HR Evolution Raman spectrometer with a laser wavelength 325 nm, respectively. A FEI Quanta FEG 250 scanning electron microscope (SEM) was used to observe the surface morphology of the specimens. After surface related tests, the specimens that were treated at 1500 °C, 1600 °C, 1700 °C, 1800 °C and 1850 °C were re-polished by BDJP-903 mirror surface grinding & polishing machine for PCD. The polishing process was done on a diamond grinding wheel with a rotation speed of 1500 r/min.

3. Results and discussions

3.1. IR transmittance

The IR transmittance spectrum of the double-sided polished diamond film is shown in Fig. 2(a). The intrinsic two- and three-phonon absorption bands are clearly observed between 4000 cm^{-1} and 1500 cm^{-1} and some nitrogen related absorption peaks can also be seen within the one-phonon region, which represent the substitutional

Table 1
Parameters of rapid heating treatment.

Treating temperature/°C	1500 ± 5	1600 ± 5	1700 ± 5	1800 ± 5	1850 ± 5	1900 ± 5	2000 ± 5
Average heating rate (≥600 °C)/°C·s^{-1}	30.4	41.4	46.7	47.6	71.1	73.3	87.5
Dwelling time at target temperature/s	30/60/90	30/60/90	30/60/90	30/60/90	30/60/90	30/60/90	30/60
H_2/Ar flow rate/L·min^{-1}	0.8/6.0	1.4/6.0	2.5/6.0	3.9/6.0	6.0/6.0	7.8/6.0	9.0/6.0
Ambient pressure/kPa	3.80	3.60	3.59	3.64	3.65	3.74	3.67
Current/A	84	85	85	85	85	85	98
Power/kW	3.95	4.68	5.78	6.89	8.33	9.27	11.47