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Synthesis of large single crystal diamond plates by high rate homoepitaxial growth using microwave plasma CVD and lift-off process

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Abstract

A process of making a large, thick single crystal CVD diamond plates has been developed. This process consists of high rate homoepitaxial growth of CVD diamond and subsequent lift-off process using ion implantation. By using this process, single crystal CVD diamond plates with the size of about $10 \times 10 \times 0.2$–0.45 mm^3 have been successfully fabricated. The crystallinity of the CVD diamond plates has been evaluated by X-ray topography, polarized light microscopy and high resolution X-ray diffraction. The results indicate the pretreatment of the seed substrate has strong effect on the crystallinity of the CVD diamond plates.

Keywords: Diamond; Microwave plasma CVD; High rate growth; Ion implantation; Lift-off; Self-standing plate

1. Introduction

To realize a large-area, single crystal diamond wafer, large bulk diamonds and their slicing technique are required. Recent developments in chemical vapor deposition (CVD) process realize high rate growth of single crystal CVD diamond faster than 10 μm/h [1–3]. These diamonds are generally grown under the high power density plasma with the high methane concentration. Especially, by adding small amount of nitrogen for the purpose of promoting (100) growth, the growth temperature can be raised up to over 1100 °C and the growth rate exceeds 100 μm/h [1,2]. This very high rate growth technique has been successfully applied to grow very thick diamonds having 10 mm in thickness and a method of further enlarging the crystal size has been proposed [4].

However, slicing a bulk diamond is still difficult because diamond is the hardest material. When a conventional cutting technique, such as sawing or laser sawing, is used, a large amount of cutting loss (>0.3 mm in thickness) will be expected for slicing such a bulk diamond into wafers. One of the promising solutions to minimize the cutting loss is to use a lift-off process using ion implantation. This process consists of ion implantation to a substrate to create a damaged layer under the surface, annealing of the substrate to convert the damaged layer into graphite and subsequent etching of the graphite layer and separation of a diamond film. This was first demonstrated by Parikh et al. [5] for removing thin diamond film from a diamond substrate. This was later used to separate homoepitaxially grown CVD diamond film grown on the ion implanted substrate [6,7]. However, the substrate size in these studies was a few mm square, and the film thickness was less than 0.1 mm which was not enough to use as a wafer.

In this work, we tried to combine the high rate CVD homoepitaxial growth process and the improved lift-off process to make a further large (10×10 mm^2) and thick (>0.2 mm) single crystal diamond plates. The crystallinity of these diamond plates was evaluated and the influence of surface pretreatment of the seed substrate prior to the CVD growth was investigated.

2. Experimental

Single crystal HPHT Ib (100) diamonds were used as a seed substrate for the process of growing and separating CVD diamond plates. Before growing CVD diamond, the substrate was

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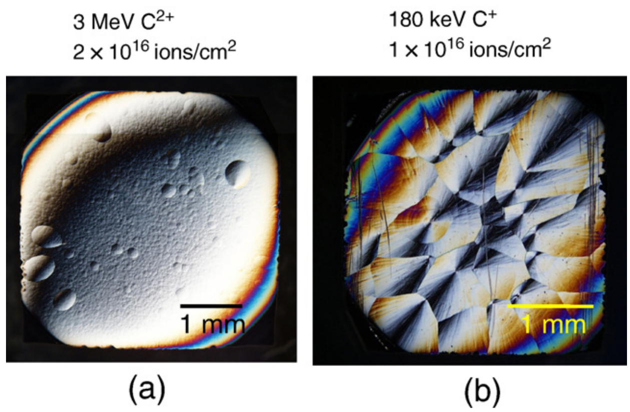

Fig. 1. DICM images of CVD diamond films grown on carbon ion implanted substrates at the energy of (a) 3 MeV and (b) 180 keV.

implanted with carbon ions at the energies of 3 MeV or 180 keV using a 1.5 MeV tandem accelerator (Nissin High Voltage NT-1500) or a 200 kV ion implanter (ULVAC IKX-3500). The projectile ranges in diamond are 1.6 and 0.22 μm, respectively.

After the ion implantation, single crystal diamond was grown on the ion implanted substrate by an ASTEX-type 5 kW CVD reactor (Seki Technotron AX-5250). The growth rate was enhanced by using a specially designed substrate holder and nitrogen addition [2,4]. The substrate temperature during the growth was 1130–1150 °C, which was measured by optical pyrometer (Chino IR-U). The pressure of the reactor was 24 kPa and the gas flow rate was 500 sccm for H_2, 60 sccm for CH_4 and 0.6 sccm for N_2. The high growth temperature is enough to convert the damaged ion implanted layer into the graphite. After the growth, the graphite layer was etched by an etching process using a similar method proposed by Marchywka et al [7].

The surface morphology of the CVD diamond plate separated from the substrate was characterized by differential interference-contrast microscopy (DICM) and atomic force microscopy (AFM). The crystallinity was evaluated by transmission X-ray topography, polarized light microscopy (PLM) and high-resolution rocking curve measurement of X-ray diffraction (XRD). The X-ray topograph was taken using Mo Kα X-rays with transmission (g=220) diffraction geometry. The X-ray rocking curves of the (004) reflection were measured by an X-ray diffractometer equipped with a Ge (440) four-crystal monochromator for Cu Kα X-rays.

3. Results and discussion

High rate growth of CVD diamond was applied to the ion implanted substrate with the different ion energies. Fig. 1 shows the surface morphology of the single crystal CVD diamond films grown on the HPHT diamond substrates implanted with carbon ions at 3 MeV and 180 keV. The ion dose should be larger than a critical dose which is necessary to lead to graphitization in the next growth (or annealing) process, but at the same time, as low as possible to minimize surface damage. In the present case, the selected ion doses were 2×10^{16} ions/cm^2 and 1×10^{16} ions/cm^2, respectively. The film thicknesses were 0.29 and 0.38 mm after 6 h growth. Both films could be successfully separated from the substrate after the etching process. However, in case of 180 keV implantation, the grown film contains many hillocks on the surface. In contrast, using high-energy (3 MeV) ion implantation, the film with smooth surface morphology is obtained. This result suggests that low surface damage created by high-energy ion implantation is beneficial for the high rate growth process. Also, the thickness of diamond above the ion implanted layer increases with increasing the range of ions. This improve the process margin at the initial stages of the CVD process where the etching of diamond can not be negligible.

The lift-off process using high-energy ion implantation was successfully applied to larger HPHT diamond substrates with the size of about 10×10 mm^2. The substrate was implanted with 3 MeV carbon ions with the dose of 2×10^{16} ions/cm^2. After the ion implantation, single crystal CVD diamond was grown on the substrate. For this purpose, a substrate holder with the upper surface diameter of 18 mm was used. Using this holder and the above-mentioned growth conditions, the typical growth rate of 30–50 μm/h was obtained over the entire (10×10 mm^2) growth area. The etching of graphite layer took typically 1–2 days, and

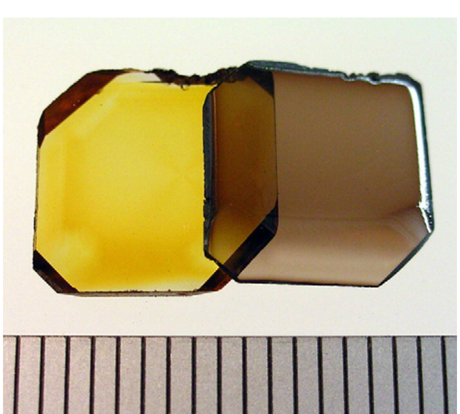

Fig. 2. A $10\times10\times0.4$ mm^3 single crystal CVD diamond plate (right) separated from a HPHT diamond substrate (left) by combination of high rate growth and lift-off process using ion implantation.

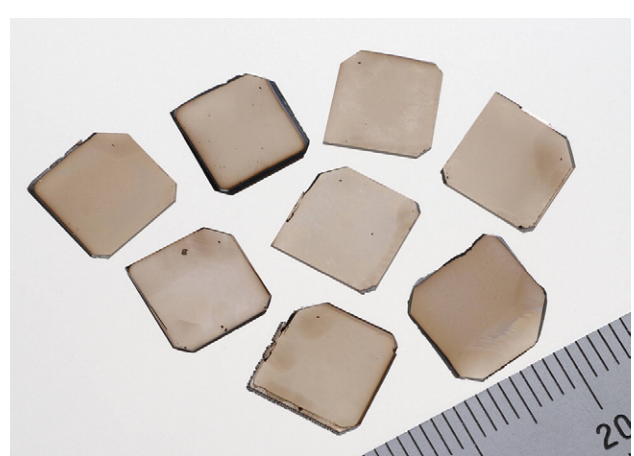

Fig. 3. Large CVD diamond plates mass-produced by combination of high rate growth and lift-off process using ion implantation.