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Fabrication of free-standing diamond membranes

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Abstract

We describe here a method for fabricating free-standing diamond membranes. Diamond films were deposited on a silicon substrate by microwave plasma-assisted chemical vapor deposition and then part of the substrate chemically removed. The films described here were 15 mm in diameter with thickness of approximately 12 μm. A novel feature of our approach lies in the method used to obtain the selective dissolution of the substrate; a container with O-rings was used, instead of masks, allowing a fast and clean isotropic dissolution of part of the silicon substrate. The deposited diamond films as well as the free-standing membranes were characterized by scanning and transmission electron microscopy, electron diffraction and Raman spectroscopy.

Keywords: Diamond; Chemical vapour deposition; Plasma processing and deposition

1. Introduction

Diamond thin films possess a number of unique chemical and physical properties that make them attractive for a broad range of applications in research and industry. The rapidly developing technology for the growth of polycrystalline diamond films by plasma-assisted chemical vapor deposition (CVD) on a range of substrates has increased interest in this material. Applications of diamond thin films include: wear-resistant coatings for cutting tools, by virtue of its hardness; as thermal management of electronic devices, because its room-temperature thermal conductivity is the highest of all materials; as free-standing windows with good transparency in the visible and infrared region; and as free-standing permeable membranes [1] for use as filters, by virtue of the chemically inert and mechanically resistant nature of diamond. Several CVD methods have been developed and successfully used to produce diamond films such as, for example, hot filament CVD [2], electron-assisted CVD [3], microwave plasma-assisted CVD [4], d.c. discharge CVD [5], and use of the oxygen-acetylene torch [6].

In this paper we describe a method for fabricating free-standing diamond membranes from a film deposited on silicon. Selective chemical etching of the substrate promotes dissolution of the silicon leaving the diamond membrane intact. The method is particularly attractive because of its simplicity, ease for producing large area membranes, and its low cost.

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2. Experimental details

The diamond films were synthesized by microwave plasma-assisted CVD using a system that has been fully described elsewhere [7]. The growth parameters used here were: 300 sccm for the hydrogen flow rate, 1.5 sccm for the

Fig. 1. Container with O-rings for dissolution of part of the silicon substrate. The sample was loaded on the lower O-ring with the diamond side down, then the upper part of the container was screwed tight so as to sandwich the sample between the two O-rings.

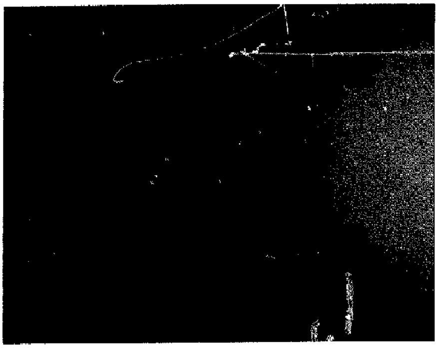

Fig. 2. The circular region inside the square (18 × 18 mm^2) silicon substrate is a free-standing diamond membrane.

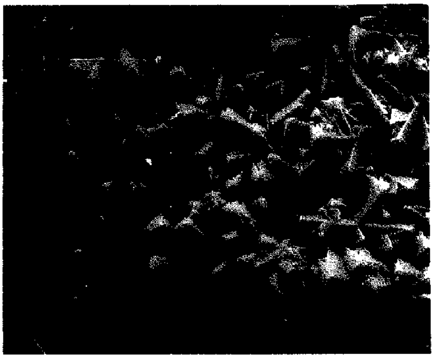

Fig. 3. SEM of the top side of the diamond membrane showing morphology typical of CVD-grown polycrystalline diamond film.

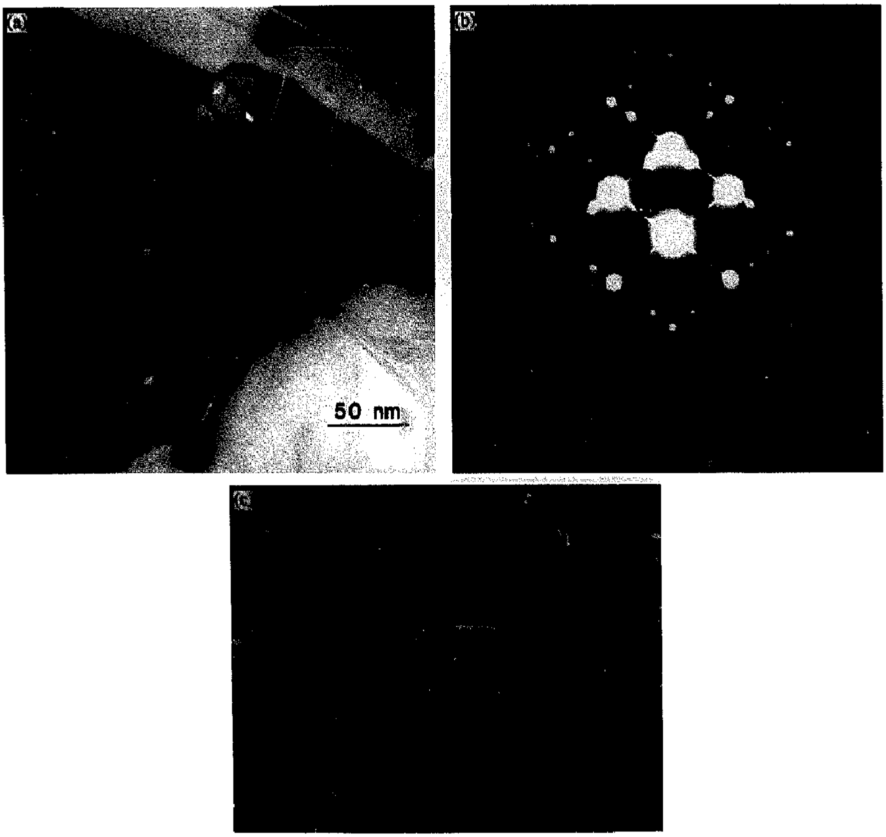

Fig. 4. (a) Bright-field transmission electron microscopy image of a diamond grain with normal parallel to [110] direction. Twin bands are indicated in the picture, and their signatures indicated in the diffraction pattern. (b) Electron diffraction pattern of the grain shown in (a). (c) High-resolution transmission electron micrograph of a CVD diamond membrane.

methane flow rate (0.5 vol.% methane), 9.3×10^3 Pa for the chamber pressure, 850 °C for the sample temperature, and a nominal 870 W for the microwave power. Film thickness was controlled by variation of the growth time between 10 and 48 h.

A novel feature of our approach lies in the method used to obtain the selective dissolution of the substrate: a container made of PVC, with Buna-N O-rings, as shown in Fig. 1, was used instead of masks, allowing a fast and clean isotropic dissolution of part of the silicon substrate. The sample (diamond film on its silicon substrate) was loaded on the lower O-ring with the diamond film down. Then the upper part of the container was screwed tight so as to sandwich the sample between the two O-rings. A room-temperature mixture of hydrofluoric acid, nitric acid and acetic acid [8] was used to dissolve the silicon. The $HF:HNO_3$ volume ratio was 2:1, and the acetic acid was added to prevent violent reaction that can fracture the diamond membrane during the substrate etching. The time required to dissolve the substrate was between 10 and 30 min for a silicon substrate of thickness of about 200 μm.

Scanning and transmission electron microscopy were used to characterize the deposited diamond films as well as the free-standing membranes. A Jeol JSM-840A scanning electron microscope (SEM) with an accelerating voltage of 25 kV was used to evaluate the surface morphology of the films, as well as the etch profile of the silicon substrate. Transmission electron microscopy (TEM) was conducted in a TOPCON 002B. At 200 kV the point resolution of this microscope is 0.19 nm, which is suitable for viewing {111} lattice fringes of diamond. Samples for TEM were prepared by mounting pieces of thin free-standing membranes (5 μm thick or less) on copper grids and ion milling the films with an Ar^+ beam at 3.5 kV until perforation occurred. Raman spectroscopy was also carried out to provide additional information on the quality of the membranes produced.

3. Results and discussion

We have in this way made a number of thin diamond membranes with the central 15 mm diameter substrate free. Note that the diameter of the free-standing region is determined simply by the O-ring size, which can readily be increased so as to prepare free-standing films of arbitrary size.

An example of one of our diamond membranes is shown in Fig. 2, where the diamond film lies within the circular region and the square silicon substrate is 18×18 mm^2. Fig. 3 shows a SEM of the top side (growth side) of the diamond film, showing morphology that is typical of polycrystalline diamond films.

The surface morphology of the deposited films consisted mainly of (111) and (100) facets. Transmission electron microscopy also indicated the presence of stacking faults, and micro- and macro-twins, which have been often observed in CVD diamond films. Fig. 4(a) shows a transmission electron micrograph of one of the membranes produced with one of the grains oriented with the electron beam parallel to the [011] direction. Observation of stacking faults and twin domains is most easily done under this conditions. In this orientation the stacking faults and twin domain boundaries, which coincide with {111} planes, are seen edge-on, and their signature on the diffraction pattern is easily identifiable. Fig. 4(b) shows the electron diffraction pattern of the grain shown in Fig. 4(a). Diffraction spots resulting from multiple twinning, and streaks resulting from stacking faults or microtwins are observed. The high resolution image of another crystal of the diamond membrane under similar orientation is also shown in Fig. 4(c). Multiple twinning and stacking faults are easily identified.

The Raman spectra of the two sides of one membrane are presented in Fig. 5. These spectra are consistent with that of diamond with very low amorphous carbon phase contamination. It is interesting to note that there is slightly more amorphous carbon at the silicon side than on the growth side.

Fig. 6 shows the back side of the sample, where the diamond film was in contact with the silicon substrate before its chemical dissolution; one can see in this micrograph that the diamond grain size is about 4 μm. Fig. 7 shows the back side of the diamond film where it adjoins the thicker silicon substrate; the smooth region on the right hand side of the figure

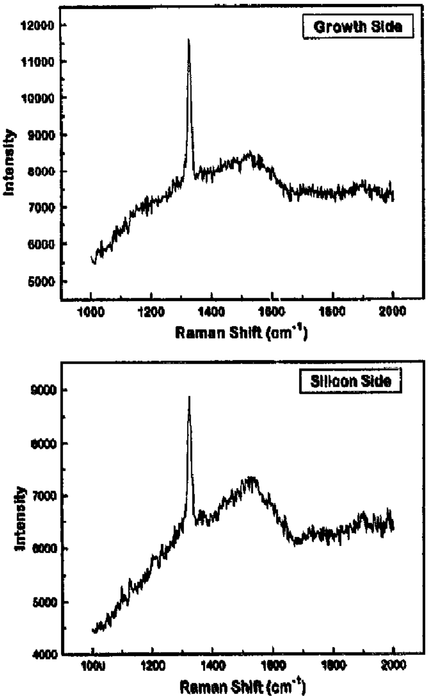

Fig. 5. Raman spectra of both sides of a free-standing diamond membrane.

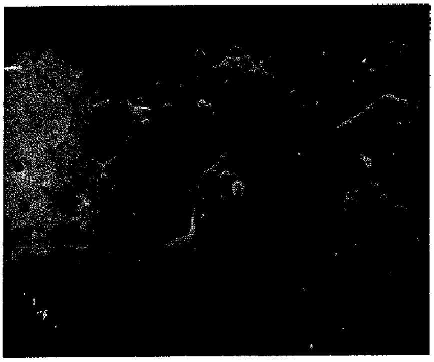

Fig. 6. SEM of the back side of the diamond membrane, where the diamond film was in contact with the silicon substrate before its chemical removal. The diamond grain structure is clearly shown.

Fig. 7. SEM of the back side of the membrane near the edge. The smooth part (right) is the free-standing diamond film and the rough part (left) is the silicon substrate.

is the free-standing diamond film and the rougher part on the left side is the silicon substrate. Note that the silicon profile near the free-standing diamond film is sharp, in spite of the fact that the chemical dissolution was isotropic. The film thickness of about 12 μm was determined by breaking a film grown under similar condition and measuring it under SEM.

4. Conclusion

We have fabricated a number of diamond membranes by selective dissolution of the silicon substrate using a container with O-rings, instead of masks, allowing a fast and clean isotropic removal of a chosen part of the substrate. The test diamond membranes, made in the work described here, were circular with a diameter 15 mm. The size of the free-standing region can readily be increased.

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