

Free-standing single-crystalline chemically vapor deposited diamond films

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Free-standing chemically vapor deposited (CVD) single-crystalline diamond films have been fabricated by a sequence of processes including high energy ion implantation, microwave plasma enhanced chemical vapor deposition, and the final separation of the diamond epilayer from the substrate by heating in oxygen. The homoepitaxial diamond film separated from the substrate is about 15 μm thick. It is flat and transparent, and exhibits a sharp diamond Raman peak without nondiamond background signals. This process is promising for mass production of large-area single-crystalline diamonds with the size restricted only by the availability of one large initial diamond substrate. The initial substrate is expensive but can be used repetitively to produce a large number of single-crystalline CVD diamond films.

Diamond is known to have excellent properties that make it attractive as a material for electronic and other device applications.¹ There has been worldwide interest in the use of vapor phase epitaxial growth techniques to obtain single-crystalline diamond films. Although some successes have been achieved in localized heteroepitaxial growth on few substrates such as single-crystalline nickel, the grown heteroepitaxial diamonds are so small that they are practically useless for device fabrication. Almost every researcher working on active diamond electronic devices presently relies on either natural diamond or high pressure/high temperature (hp/ht) diamond substrates that are very expensive, especially when the size exceeds a few mm. For larger sizes, single-crystalline diamond is either not available or is very rare and cannot be used for reproducible fabrication of a large number of active electronic devices. This makes it urgently necessary for us to develop methods that are different from heteroepitaxial diamond growth while still capable of producing affordable single-crystalline diamonds of reasonable sizes.

Unlike heteroepitaxial growth of diamond, homoepitaxial growth of diamond on single-crystalline diamond substrates by means of various chemical vapor deposition techniques² has become a routine process. The goal of this work is to grow thick homoepitaxial diamond films on single-crystalline diamond substrates so that the diamond epilayers can be separated from the substrates leaving the substrates for repetitive uses. The repetitive use of the same substrate makes it affordable to use an expensive diamond substrate of a large area. Two approaches have been pursued. The first one involves an etch-stop epitaxial interlayer between the diamond substrate and the diamond epilayer. At the time of writing this letter, no conclusive success has been achieved for this process yet. The second approach is based on the fact that high energy (MeV) ions cause little damage to the diamond crystalline structure. After ions lose energy on their way into the diamond, they reach a lower energy at which the diamond crystalline structure

can be severely damaged. Therefore, a high energy ion beam can be used to implant into a diamond substrate in order to create a damaged layer under the diamond surface leaving the diamond surface practically intact. The distance from the damaged underlayer to the diamond surface is determined by the initial energy of the ion beam.

In a recent letter by Parikh *et al.*,³ the separation of a very thin (1–2 μm) diamond surface layer from a diamond substrate was reported using this process. The separated diamond film had been subjected to ion beam irradiation and was black in color and curled up due to internal stress. No Raman spectra or other further characterization results were reported.

Shown in Fig. 1 are the calculated ion trajectory, range, and ion induced vacancies for implanting a 3.7-MeV O^+ ion beam into a diamond substrate. The calculation was based on the Kinchen–Pease model using the TRIM code. As can be seen in this figure, most of the damages occur at a distance of more than 1 μm from the diamond surface. The diamond surface is almost free of ion beam induced damages, and thus can be used for further homoepitaxial growth of a diamond film.

In order to achieve a free-standing single-crystalline diamond film, the ion implanted diamond substrate must withstand the same conditions for the homoepitaxial diamond growth while retaining the ion damaged underlayer. If the implantation dose is too high, the diamond film will break apart from the substrate prematurely during the high temperature growth. On the other hand, the chemically vapor deposited (CVD) diamond cannot be separated from the substrate after the growth process if the implantation dose is too low.

This letter reports, for the first time, that a homoepitaxial diamond film grown on an ion implanted diamond substrate was successfully separated from the substrate. The free-standing single-crystalline diamond film was analyzed by means of Raman spectroscopy on both sides of the diamond epilayer as well as on the front surface of the

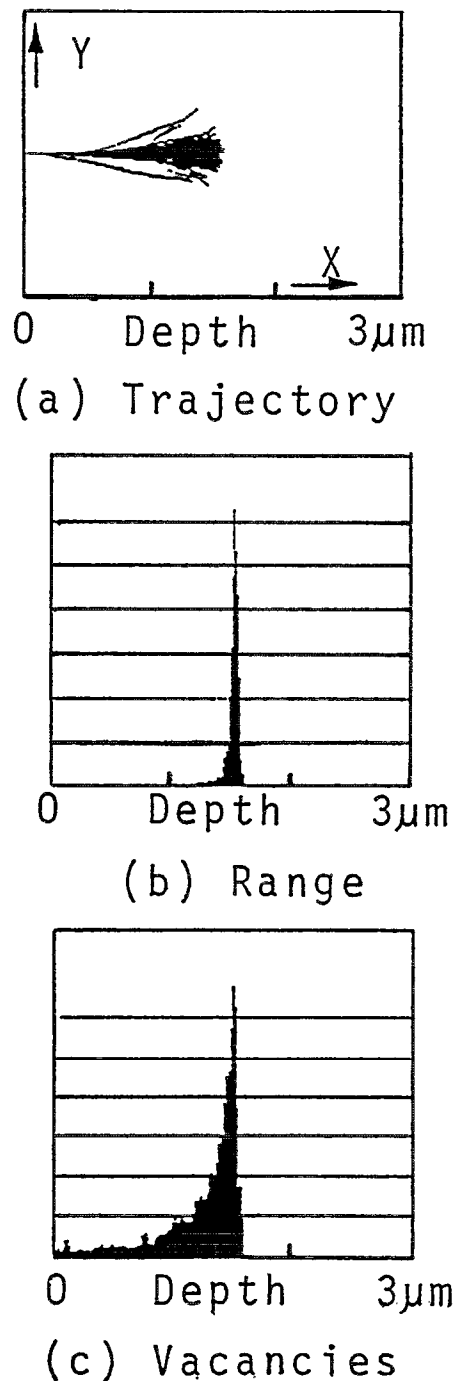


FIG. 1. Calculated ion beam (a) trajectory, (b) range, and (c) induced vacancies in a diamond substrate by a 3.7-MeV O^+ ion beam.

substrate after separation. Oxygen ion beams of 3.5–5 MeV were used for the implantation into natural and synthetic single-crystalline diamond at doses ranging from 1×10^{17} to $1 \times 10^{18} \text{ cm}^{-2}$ at either the room temperature or the liquid nitrogen temperature. The ion implanted diamond substrates were then loaded into a microwave plasma enhanced chemical vapor deposition reactor for homoepitaxial diamond growth. The growth was carried out in 1.5% CH_4 diluted by hydrogen at a substrate temperature between 800 and 900 °C and at a gas pressure of

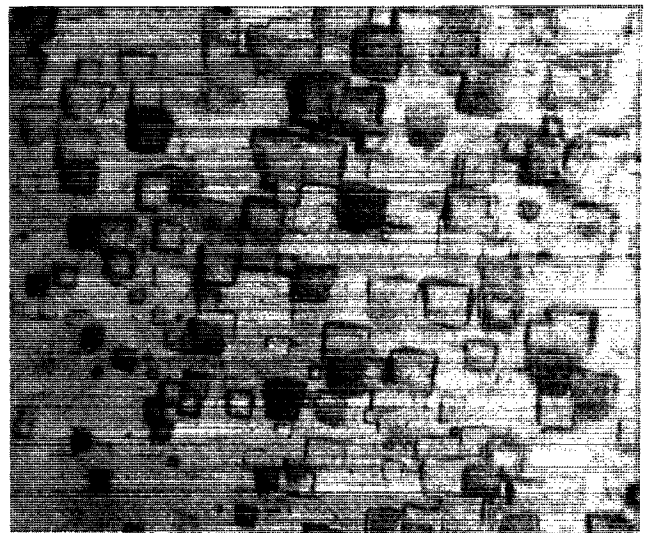


FIG. 2. Nomarski phase contrast optical micrograph of the surface of a homoepitaxial diamond film grown for 15 h on a high energy ion beam implanted type IIA natural diamond substrate.

50 Torr. The microwave power was 600 W. Usually, it takes ~15–20 h of growth to achieve from 10- to 20- μm -thick diamond epilayers. Shown in Fig. 2 is the Nomarski phase contrast optical micrograph of a diamond homoepitaxial layer grown on ion implanted (100) oriented type IIA natural diamond. The surface morphology of the (100) oriented diamond epilayer can clearly be seen in this photograph.

The freshly grown diamond homoepitaxial layer on a diamond substrate implanted at a dose of $3 \times 10^{17} \text{ cm}^{-2}$ by 3.7-MeV oxygen ions was then loaded into a chamber and

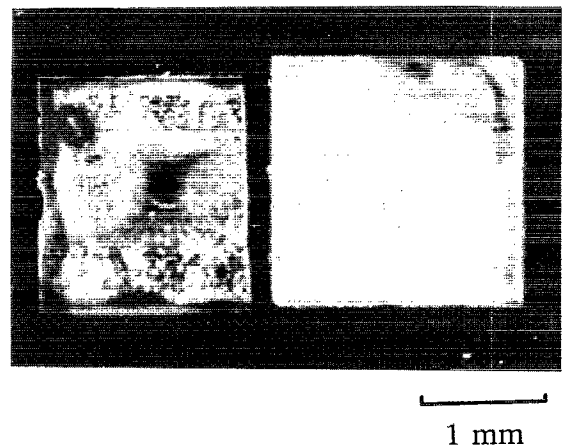


FIG. 3. Optical micrograph of a free-standing chemically vapor deposited single-crystalline diamond (left) separated from the natural diamond substrate (right) by means of preferential oxidation of a damaged layer under the surface of the diamond substrate caused by a predeposition implantation at a dose of $3 \times 10^{17} \text{ cm}^{-2}$ by 3.7-MeV oxygen ions.

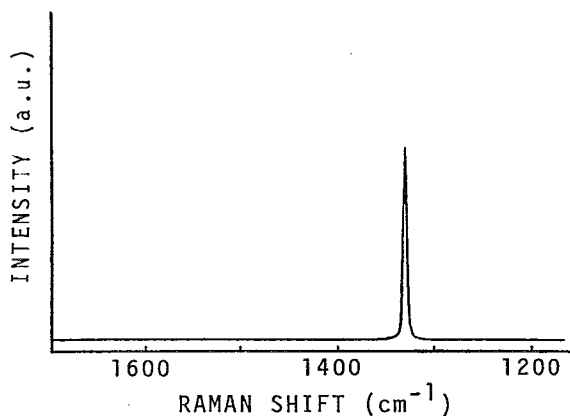


FIG. 4. Raman spectrum of a free-standing single-crystalline diamond film separated from the substrate. The spectrum was taken from the growth side of the film.

resistively heated to 600 °C in oxygen at 1 atm for 5–6 h to complete the separation of the epilayer from the substrate. Figure 3 shows a separated single-crystalline diamond film and the original substrate. This free-standing diamond film is flat and transparent. It is about 15 μm thick. The surface of the epilayer was not subjected to ion beam irradiation. A Raman spectrum taken on the growth surface of the separated diamond epilayer is shown in Fig. 4. The presence of a sharp diamond Raman peak and the lack of other nondiamond background signals indicate that the diamond epilayer is of high quality. On the other hand, the Raman spectra for the back side of the diamond epilayer and the front side of the diamond substrate after separation all have a diamond peak superimposed with a broad graphite spectrum as shown in Fig. 5. This indicates

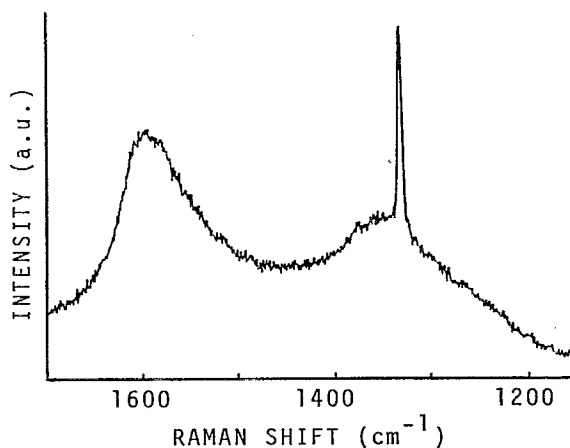


FIG. 5. Raman spectrum of a free-standing single-crystalline diamond film separated from the substrate. The spectrum was taken from the substrate side of the film.

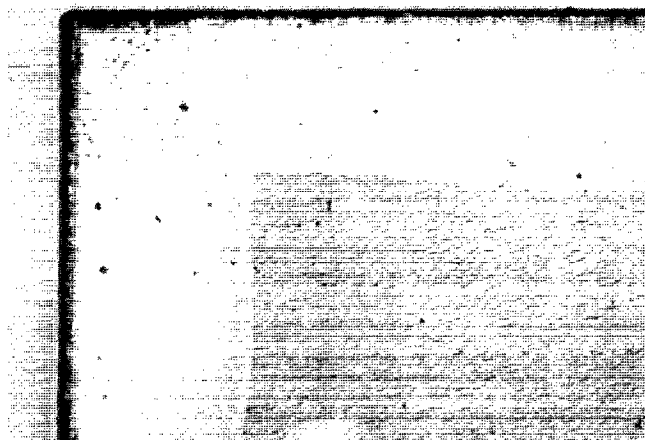


FIG. 6. Optical micrograph of a partially separated diamond epilayer on a type IIA natural diamond after 2 h heating in oxygen at atmospheric pressure.

that the ion beam damaged underlayer was converted into graphite during the diamond homoepitaxial growth and the heating process in oxygen. Shown in Fig. 6 is a partially separated specimen after 2 h of oxidation in oxygen. The partial removal of the graphitized underlayer appears as a clear region near the edge of the specimen. This transparent region expands with increasing heating time in oxygen until the epilayer is completely separated from the substrate.

We have successfully demonstrated, for the first time, the fabrication of a free-standing single-crystalline diamond made by the microwave plasma enhanced chemical vapor deposition technique on an ion implanted diamond substrate followed by a separation process. This technique is believed to be up-scalable for producing large-area single-crystalline diamond as long as the first single-crystalline diamond substrate is available.

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¹ See references in *Applications of Diamond Films and Related Materials*, edited by Y. Tzeng, M. Murakawa, M. Yoshikawa, and A. Feldman (Elsevier, Amsterdam, 1991).

² Y. Sato, I. Yashima, H. Fujita, T. Ando, and M. Kamo, in *New Diamond Science and Technology*, edited by R. Messier, J. Glass, J. Butler, and R. Roy (Materials Research Society, Pittsburgh, PA, 1991), p. 371.

³ N. R. Parikh, J. D. Hunn, E. McGucken, M. L. Swanson, C. W. White, R. A. Rudder, D. P. Malta, J. B. Posthill, and R. J. Markunas, *Appl. Phys. Lett.* **61**, 3124 (1992).