Ion-Beam-Assisted Lift-Off Technique for Three-Dimensional Micromachining of Freestanding Single-Crystal Diamond**

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Diamond is a very attractive material for micromachining: it has high mechanical hardness, high Young’s modulus, a low coefficient of friction, high thermal conductivity, and a low thermal expansion coefficient. It is chemically inert and bio-compatible. Optically, it is transparent over the widest range of the electromagnetic spectrum (from 220 nm to the far infrared), has a high refractive index, and exhibits a vast inventory of luminescent centers (>500 electronic, >150 vibrational), many of which are related to impurities or defects in the crystalline structure.[1] Some of these can therefore be controlled and engineered. Of particular interest is the nitrogen vacancy (NV–) center that possesses very promising quantum properties.[2]

At present, despite the prospects for such luminescent centers, no fabrication schemes have been demonstrated for integrated microphotonic devices in diamond. The micromachining of three-dimensional structures in bulk diamond is technologically challenging,[3–6] therefore, most existing techniques are based on the use of chemical vapor deposition (CVD) of polycrystalline films combined with selective ablation or replication processes that employ masking and molding. Previous work reports the use of such methods to produce scanning probe tips and cantilevers,[3] field emitters,[4] microelectromechanical systems (MEMS),[5] nanoelectromechanical systems (NEMS),[6] and microfluidic channels.[7] Two-dimensional microstructures (holes and trenches) can be drilled in single crystals by means of high-power laser ablation.[8,9]

 Compared to single-crystal diamond, CVD polycrystalline diamond has poor optical transparency and inferior and less-reproducible mechanical properties. This constitutes a limitation for many technological applications. Here we report a new method for the fabrication of freestanding microstructures in bulk single-crystal diamond. The method takes advantage of the fact that ion irradiation of diamond followed by thermal annealing induces a phase transformation to amorphous carbon, which can be selectively etched to leave freestanding diamond structures. We also report the construction of an optical waveguide structure integrated with total internal reflection mirrors, constituting the first waveguide fabricated in single-crystal diamond. Potential applications of this technique are in the development of fully integrated quantum photonic devices employing photoluminescent centers in diamond, and in the field of MEMS, microfluidics, and biophysics.

Our method is inspired by the diamond lift-off technique, which was initially developed as a method to remove thin layers from bulk diamond samples.[10] The present work is based on MeV ion implantation followed by thermal annealing to create a buried sacrificial layer at a well-defined depth. Patterned milling with a focused ion beam (FIB) is then used to expose defined regions of the sacrificial layer to selective chemical etching and subsequent lift-off. A final thermal-annealing step is employed to remove residual damage produced in the fabrication. We now briefly discuss each of these steps.

MeV Ion Implantation: Type Ib “Sumicrystal” diamonds were implanted with 2 MeV He ions at a fluence of $1.5 \times 10^{17}$ ions cm$^{-2}$ in localized regions of nominally 100 $\mu$m $\times$ 100 $\mu$m, as shown in Figure 1a. MeV ion implantation induces the creation of lattice defects (i.e., vacancies and interstitials) resulting from the collisions with atomic nuclei. The maximum rate of nuclear-energy loss of light ions occurs when the ion energy decreases to $\sim 102$ eV, that is, at the end of range of the MeV ions,[11] thus resulting in the formation of a buried, highly damaged layer. The depth and thickness of the damaged layer can be controlled with submicrometer spatial resolution with a proper choice of ion species and energy. A buried heavily damaged layer is created at a depth of $\sim 3.5$ $\mu$m below the surface, while the region between the surface and the end of range exhibits a much lower damage density. The heavily damaged layer forms a sacrificial layer for subsequent etching.

Micropatterning: Following MeV ion irradiation, the samples were patterned with a FIB employing a 30 keV gallium ion beam with submicrometer size. The focused ion beam milled micrometer-width linear trenches deep enough to ex-

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pose the buried highly damaged layer to the surface. The focused beam was scanned to define patterns as shown in Figure 1b. We note that 1 μm spatial resolution machining of diamond can also be achieved with high-power laser ablation.

Other possible manufacturing techniques include conventional photolithography, masking with a hard mask such as a deposited metal, and reactive-ion etching (RIE) in oxygen. However, the focused ion beam can machine trenches a few tens of nanometers in width and therefore allows, in principle, the fabrication of nanometer-sized structures in single-crystal diamond.

**Thermal Annealing:** After the FIB patterning, the samples were thermally annealed at $T = 550 \, ^\circ C$ in air for 1 h. The damage density threshold, beyond which diamond structure is not recovered upon annealing, is reported to be $1 \times 10^{22}$ vacancies cm$^{-3}$.[12,13] Therefore, after the annealing process only in the highly damaged layer (which is exposed to the surface through the FIB-machined trenches), the crystal structure is converted to tetrahedral amorphous carbon, while in the less-damaged regions the diamond structure is recovered.

**Etching:** The annealed samples were processed via wet chemical etching in boiling acid (1:1 H$_2$SO$_4$/HClO$_4$/HNO$_3$). The chemical attack selectively etches the exposed sacrificial layer, while leaving intact the chemically inert diamond phase. It can be observed in Figure 1c that the process starts at the corners of the patterned region, where the trenches intersect, thus forming deeper and wider drilled regions. Buried damaged regions connected to a trench but otherwise covered by undamaged diamond are also etched allowing unconnected surface layers to lift off, leaving behind the desired patterned structure, which may include under-etched (i.e., freestanding) regions. An example of such a freestanding structure is the cantilever shown in the SEM image in Figure 1d. With the same procedure, freestanding bridges can be created, as shown in Figure 2. The structures have well-defined submicrometer-sized features, and the bottom surface after the lift-off appear very regular and smooth; surface roughness measurements performed with atomic force microscopy (AFM) confirm that its root-mean-square (RMS) roughness is $\sim 2$ nm, equal to that of the original diamond surface. This is due to the abrupt damage threshold for phase transformation upon annealing that leads to a sharp interface between diamond and the sacrificial layer.

**High-Temperature Annealing:** A final thermal-annealing step was employed to recover the pristine diamond structure from residual damage induced from both MeV He and stray keV Ga ions in the implantation and patterning steps, respectively. The samples were annealed for 2.5 h at a temperature of $1100 \, ^\circ C$ in forming gas (4% H$_2$ in Ar), which allows annealing whilst preventing high-temperature oxidation. Previous work reported that this annealing strategy causes most of the ion-induced damage to be removed and the crystalline diamond structure to be recovered.[13] This is confirmed by Raman characterization of the samples: Raman spectra exhibit clear diamond features and low residual damage in the annealed microstructures.

**Total Internal Reflection Mirrors:** To inject light into our structures, we developed an input/output light-collection system based on linear trenches inclined at 45° with respect to the

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**Figure 1.** Microfabrication process of a cantilever structure in single-crystal diamond: a) MeV ion implantation (optical image of the 100 μm×100 μm implanted regions) is followed by b) FIB-micromachining (scanning electron microscopy (SEM) image of the patterned trenches), thermal annealing, and c) chemical etching (optical image of the structure after subsequent etching steps progressively undercutting the cantilever); d) shows a SEM image of the final cantilever structure.

**Figure 2.** SEM image of a micrometer-scale bridge structure machined in single-crystal diamond; the $\sim 400$ nm thick gap below the freestanding bridge is visible.
sample surface. The mirrors, as shown schematically in Figure 3a, exhibit total internal reflection (TIR) owing to the difference in the refractive index of diamond with respect to air. The refractive index of diamond at a wavelength of $\lambda = 532 \text{ nm}$ is $n = 2.43$, and the critical angle is $i_c = 25^\circ$. To fabricate the mirrors, linear trenches were milled with the FIB at a depth of 5 $\mu$m by tilting the sample at the desired angle. The sample was then processed with the annealing and etching steps described above. The as-machined mirrors are completely opaque, and the annealing and etching processes, which remove the amorphous materials and smooth the surface after the FIB machining, are essential for the mirrors to function correctly.

The transmission of light in the device was investigated by fabricating mirrors at each end of the bridge structure and focusing $\lambda = 532 \text{ nm}$ laser light with a long-distance optical objective to a micrometer-sized spot at the input mirror. The collection of the transmitted light from the output mirror was performed with the same objective, as shown schematically in Figure 3b. The results of the test in the bulk crystal are shown in Figure 3c: no light is detected along the path between the two mirrors because of the low scattering. It can be observed that the outgoing light is spread along the whole extension of the output mirror, although the incoming beam is focused at the input mirror. This is due to the divergence of the light focused on the first mirror. When the light is coupled through the bridge via the input and output mirrors, it is waveguided, as shown in Figure 3d; this is confirmed by the complex modal pattern observed at the output mirror highlighted in Figures 3e,f. The resulting pattern can be attributed to the constructive and destructive interference of modes propagating along the waveguide. Because the structure is relatively large (with cross-dimensions $\sim 2 \mu$m × 3.4 $\mu$m), with the diamond refractive index of $n = 2.43$, the propagation is highly multimoded, and we estimate that more than 10 propagation modes are present.

In principle, the present machining technique allows the creation of smaller single-mode waveguides, which represent the ideal tool for microphotonics applications. A single-mode waveguide is therefore a future goal of this research; however, in the present case a highly multimodal structure was fabricated that allowed ready identification of the waveguiding behavior. Future work will be devoted to the optimization of the machining technique, especially as regards the removal of residual damage. We note that even more complex three-dimensional structures could be fabricated by employing multiple MeV ion-implantation steps each with different energies to create multiple sacrificial layers at different depths. It is also possible to employ a higher-resolution FIB to produce smaller and more sophisticated optical elements including beam-splitters, single-mode waveguides, and optical cavities. This method has also a great potential for the production of micro-resonators, beams for integration in MEMS with waveguide sensing, and whole classes of new high-performance devices: it represents the ideal toolkit for the production of fully integrated micromechanical assemblies and nano-optics devices in diamond.

**Experimental**

MeV Ion Implantation: Type Ib diamonds produced by Sumitomo (high-pressure, high-temperature (HPHT) single crystals with a dispersed nitrogen concentration of 10-100 ppm) were implanted with 2 MeV He$^+$ ions on the MP2 microbeam line of the 5U NEC Pelletron accelerator at the University of Melbourne. The beam was focused to a micrometer spot and scanned with magnetic coils in order to get optimal homogeneous ion fluence. The beam current was about 9 nA; therefore, the implantation of a 100 $\mu$m × 100 $\mu$m region required 4.5 min to achieve a fluence of $1.5 \times 10^{17}$ ions $\text{cm}^{-2}$.

FIB Micropatterning: This was performed using a Cauion 31M plus FIB by Orsay Physics mounted on a JEOL-5910 SEM and equipped with a Raith Elphy Quantum ion-beam lithography package for the automated machining of user-defined patterns. The FIB provided a 30 keV Ga$^+$ ion beam with a current $\sim 2.7$ nA. A rough estimation of the diamond machining rate for our experimental conditions was...
−0.1 μm² nC⁻¹, compared to −0.15 μm² nC⁻¹ in silicon. Greatly increased FIB etch rates could be achieved with water-vapor assistance.

**Thermal Annealing:** The intermediate and final annealings were performed in a furnace, in a controlled atmosphere. The intermediate annealing was at 550 °C for 1 h in air, while the final annealing was at 1100 °C for 2.5 h in forming gas (4 % H₂ in Ar), where the hydrogen in the annealing gas prevented high-temperature oxidation.

**Etching:** The samples were etched in boiling acid (1:1:1 H₂SO₄/HClO₄/HNO₃) and then rinsed in hot water and isopropyl alcohol to avoid thermal shocks to the microstructures. When the sacrificial layer was completely undercut, the sample was rinsed for few minutes in an ultrasonic bath in order to allow the lift-off of the sacrificial layer without damaging the microstructures.

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**Control of Carrier Density by a Solution Method in Carbon-Nanotube Devices**

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Single-walled carbon nanotubes (SWCNTs) are prospective components of nanoscale and molecular electronic devices.[1] For instance, field-effect transistors (FETs) have been successfully fabricated from single semiconducting SWCNTs.[2–3] Their mobilities can be as high as 100 000 cm²Vs⁻¹,[4] and ON/OFF current ratios can be larger than 10⁶.[5] Recently, with palladium as the electrode material, Schottky-barrier-free ballistic FETs have been realized, exhibiting high drive currents, excellent transconductance, and switching ratios of 10⁶.[6] These favorable intrinsic electrical characteristics make single-SWCNT devices potentially attractive for a range of applications, for example, in the emerging fields of flexible plastic electronics and macroelectronic systems, where large collections (arrays or random networks) of SWCNTs form effective semiconductors in thin-film transistors and diodes.[6–11]

For further evolution of SWCNT electronics, Fermi-energy engineering of carrier type and density in air are important for constructing complementary electronics that are known to be superior in performance (for example, low power) to devices consisting of unipolar p- or n-type transistors. In general,