Deterministic Nanopatterning of Diamond Using Electron Beams

James Bishop, Marco Fronzi, Christopher Elbadawi, Vikram Nikam, Joshua Pritchard, Johannes E. Fröch, Ngoc My Hanh Duong, Michael J. Ford, Igor Aharonovich, Charlene J. Lobo, and Milos Toth

School of Mathematical and Physical Sciences, University of Technology, Sydney, P.O. Box 123, Broadway, Sydney, New South Wales 2007, Australia

International Research Centre for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi’an Jiaotong University, Xi’an 710049, Shaanxi, China

Supporting Information

ABSTRACT: Diamond is an ideal material for a broad range of current and emerging applications in tribology, quantum photonics, high-power electronics, and sensing. However, top-down processing is very challenging due to its extreme chemical and physical properties. Gas-mediated electron beam-induced etching (EBIE) has recently emerged as a minimally invasive, facile means to dry etch and pattern diamond at the nanoscale using oxidizing precursor gases such as O2 and H2O. Here we explain the roles of oxygen and hydrogen in the etch process and show that oxygen gives rise to rapid, isotropic etching, while the addition of hydrogen gives rise to anisotropic etching and the formation of topographic surface patterns. We identify the etch reaction pathways and show that the anisotropy is caused by preferential passivation of specific crystal planes. The anisotropy can be controlled by the partial pressure of hydrogen and by using a remote RF plasma source to radicalize the precursor gas. It can be used to manipulate the geometries of topographic surface patterns as well as nano- and microstructures fabricated by EBIE. Our findings constitute a comprehensive explanation of the anisotropic etch process and advance present understanding of electron-surface interactions.

KEYWORDS: nanofabrication, directed lithography, diamond, electron beam-induced etching, patterning, chemical rate kinetics, anisotropy

Diamond is a material of choice for many applications due to its extreme chemical stability, high thermal conductivity, and excellent acoustic and optical properties. To this extent, diamond has been explored in the context of emerging quantum photonic technologies, nonlinear optics, microelectromechanical systems (MEMS), acoustic devices, and electrochemistry. It also holds promise for improving the performance of more conventional electronic devices. However, due to its high chemical stability, it remains challenging to etch and nanostructure diamond in a minimally invasive manner that does not compromise the functionality of device-grade optoelectronic materials.

For many of those applications, controlling the diamond surface is of paramount importance. For example, inducing controlled patterning to expedite neuron growth on diamond surfaces has been a long-standing goal in exploiting diamond in biosensing applications. For photonic applications, enhancing light extraction by ameliorating the diamond surface via direct patterning of cones can also be advantageous. Exposing particular surfaces (e.g., {111} over {100} planes) can be a viable method to enhance incorporation of color centers. Finally, emerging applications of diamond in electrochemistry and catalysis are only in their infancy, and morphology control by direct surface patterning can be highly beneficial to improve final device performance.

Electron beam-induced etching (EBIE) has recently emerged as a versatile technique that can be used to etch diamond with no damage detected by Raman and photoluminescence spectroscopy. The technique is capable of single step, beam-directed chemical etching of a broad range of materials with high spatial resolution (~10 nm). Etching proceeds through material volatilization pathways driven by electron irradiation in the presence of a precursor.
gas and is typically performed using a scanning electron microscope (SEM). Diamond is usually etched using O₂ or H₂O precursor gases, and most studies of EBIE report etching that is isotropic. However, we recently demonstrated that H₂O EBIE of single crystal diamond is anisotropic and, as a result, yields nanostructured topographic surface patterns. In the same study, it was shown that the pattern geometry is governed by the symmetry of the crystal lattice and the chemical species of the precursor molecules. However, the origin of the anisotropy remains a matter of debate, and the roles of different gas molecules and molecule fragments at the diamond surface are unknown.

In the present study we use a combined experimental and density functional theory (DFT) approach to explain the roles of hydrogen and oxygen in EBIE of diamond. We show that the operation, and an external gas delivery system enables precise control of the etch pits and other patterns. In Figure 1, each etch pit was made by scanning the electron beam in a rectangular raster pattern. R_p designates the ratio of the H₂ to the O₂ partial pressure, which was varied from pure O₂ (Figure 2a) to a value of 8.6 (Figure 2g) by controlling the flow rates of the individual precursor gases. In addition, Figure 2h,i shows etch pits fabricated using pure H₂ and pure H₂O, respectively. The latter is included here for reference and shows the topographic patterns reported in our prior work on H₂O EBIE of diamond.

Using pure O₂ (R_p ≈ 0), we observe a “sponge-like” surface texture at the etch pit base (Figure 2a), and the morphological features are not aligned with crystallographic directions. The lack of pattern formation shows that O₂ EBIE gives rise to isotropic etching of diamond. As hydrogen is added to the system (increasing R_p in Figure 2), we observe surface patterns comprised of features aligned with crystallographic directions. This is indicative of anisotropic etching caused by variations in the etch rate (i.e., selectivity) of different crystal planes. The etch frames are aligned with the edge of the diamond prior to EBIE such that all etch pit sidewalls are approximately parallel to (100) directions. At low R_p values (corresponding to small amounts of H₂), we observe square and rectangular patterns (Figure 2b,c) which evolve toward octagonal patterns at elevated R_p values (Figure 2d–g). In pure H₂ (R_p → ∞), the pattern edges are aligned at 45° with respect to (100) crystal directions (Figure 2h).

Electron irradiation of diamond in the presence of the inert gases N₂ and Ar did not give rise to etching (see SI Figure 3), and we attribute prior reports of EBIE by these gases to the effects of residual H₂O demonstrated previously. While pure H₂ gives rise to etching of diamond, the etch rate is very low compared to that of O₂ EBIE (under equivalent conditions), indicating that the etch pathway is significantly less efficient. We obtained an etch rate of 0.32 μm²/min for O₂ and 0.06 μm²/min for H₂ (see SI Figure 4), under our experimental conditions (detailed in Methods). Using H₂O as precursor (Figure 2i), octagonal patterns form similar to those fabricated using a mixture of H₂ and O₂ at R_p = 1.67. However, the etch rate is significantly lower with H₂O than with O₂ as can be clearly seen in Figure 2 and SI Figure 4 (the same beam conditions and etch times were used for all pits, and all single precursor etch pits were fabricated using the same total pressure).

The geometries of the observed topographic patterns that form are dictated by the slowest etching crystal plane(s). During anisotropic chemical etching, material is removed primarily along direction(s) normal to the fast etching planes.
As a result, etch fronts propagate preferentially along these fast etching directions \( \langle 110 \rangle \) and expose slow etching planes which then act as a barrier to inhibit etch front propagation. Large regular features with smooth faces composed entirely of the slowest etching plane are expected if etching is continued for a sufficient amount of time.\(^{46}\)

A crystallographic analysis of the patterns formed in the etch pits of Figure 2 is presented in Figure 3. Using pure \( \text{O}_2 \), no patterns are observed and etching is isotropic, while the addition of hydrogen gives rise to the formation of planes of the \( \langle 110 \rangle \) family. We refer to these patterns as \( \langle 110 \rangle \) basis. As \( R_p \) is increased, planes of the \( \langle 111 \rangle \) family are partially formed with \( \langle 110 \rangle \) family. We refer to these patterns as \( \langle 110 \rangle \) basis. As addition of hydrogen gives rise to the formation of planes of the \( \langle 111 \rangle \) family (\( \langle 110 \rangle + \langle 111 \rangle \)) and formed by \( \langle 111 \rangle \) planes. As \( R_p \) is increased, the \( \langle 111 \rangle \) family is partially formed with edges aligned with \( \langle 110 \rangle \) directions (45° to \( \langle 100 \rangle \) directions). This results in the octagonal patterns observed at higher \( R_p \). We refer to these patterns as \( \langle 110 \rangle + \langle 111 \rangle \)’ basis. It must be noted that while smooth \( \langle 110 \rangle \) planes do form, \( \langle 111 \rangle \) planes always appear rough and partly etched. As \( R_p \) is increased further toward infinity, \( \langle 111 \rangle \) planes contribute increasingly to the patterns. Using pure \( \text{H}_2 \), the majority of edges in the patterns are aligned with \( \langle 110 \rangle \) directions and formed by \( \langle 111 \rangle \) planes. We refer to these patterns as \( \langle 111 \rangle \) basis. However, even with pure \( \text{H}_2 \) large smooth \( \langle 111 \rangle \) planes do not form.

**Role of a Remote Plasma in EBIE of Diamond.** In this section we elucidate the roles of a remote plasma on EBIE performed using \( \text{O}_2, \text{H}_2 \), and \( \text{H}_2\text{O} \) precursor gases and on residual \( \text{H}_2\text{O} \) contaminants. The patterns discussed up to this point were fabricated by EBIE performed in the presence of a remote plasma which serves to radicalize the precursor gas, but does not give rise to etching in the absence of the electron beam (see SI, section 1.5).

If the plasma is used to precondition the SEM chamber and the sample, but extinguished during EBIE, \( R_p \)-dependent pattern evolution is observed, but the effects of hydrogen are less pronounced as is illustrated by Figure 4. For pure oxygen (\( R_p \approx 0 \), Figure 4a), we observe the “sponge-like” morphology that is characteristic of isotropic \( \text{O}_2 \) etching under anhydrous conditions. However, the addition of \( \text{H}_2 \) has a lesser effect on the surface texture than when the precursor gas mixture is radicalized by a plasma. Specifically, a “sponge-like” morphology is observed even when \( R_p \approx 0.26 \) (Figure 4b), which is a condition at which \( \langle 110 \rangle \) basis patterns are observed in the presence of a remote plasma (Figure 2b).

At higher hydrogen partial pressures, \( \langle 110 \rangle \) basis patterns do occur even in the absence of a plasma, but we observe no \( \langle 111 \rangle \) contributions to the patterns even with pure \( \text{H}_2 \) (compare Figure 2f and 2h). These results confirm that the plasma enhances the effects of hydrogen on pattern formation, which we attribute to the generation of highly reactive hydrogen radicals in the precursor gas. Conversely, when \( \text{H}_2\text{O} \) is used as the precursor gas, the patterns appear to be unaffected by the plasma (see Figure 2i and Figure 4g), as is the case for pure \( \text{O}_2 \) (see Figure 2a and Figure 4a). This is attributed to the higher reactivity and surface coverages of these gases which enhanced their efficacy as precursors for electron-stimulated surface reactions.

A reference electron exposure was performed in high vacuum using the same electron beam parameters and exposure time in
order to illustrate the role of residual H2O in the experiments. Very slow etching is observed, seen as roughening of the diamond surface (Figure 4h), consistent with etching mediated by low levels of residual H2O. High-magnification images of the surface reveal patterns similar to those produced when H2O is used intentionally as an etch precursor gas, albeit on a smaller scale. The high-vacuum irradiation (Figure 4h) was performed after H2 EBIE (Figure 4f) and prior to the intentional introduction of H2O (Figure 4g), confirming that the surface morphology generated by pure H2 seen in Figure 4f is not an artifact of residual H2O.

Finally, we show directly that the above effects of residual H2O can affect O2 EBIE and H2 EBIE and that the effects of H2O contaminants can be suppressed by igniting a remote plasma either before or during etching. We start with O2, and, critically, in this experiment we did not ignite the plasma before we performed O2 EBIE (in contrast to the experiment shown in Figure 4). The {110} basis patterns are observed during O2 EBIE (Figure 5a), which are indicative of etch kinetics that are affected by residual H2O (despite overnight pumping to a base pressure of $\sim 3.0 \times 10^{-6}$ mbar prior to EBIE and the use of a cold trap on precursor gas delivery lines during etching).

We then ignited the plasma and performed the same experiment, obtaining the sponge-like texture (Figure 5b) that is characteristic of O2-mediated EBIE under anhydrous conditions (see Figure 2a). The same etch morphology was observed for several hours after the plasma was extinguished, demonstrating that an O2 plasma can be used prior to etching to temporarily suppress the effects of residual water.

The experiment was then repeated with H2 precursor gas, showing that {110} and {111} basis patterns are observed in the absence (Figure 5c) and the presence (Figure 5d) of a remote plasma, respectively. The results confirm that a remote plasma can be used to activate chemically stable gases and enable their use as precursors for electron stimulated surface processing.

Role of Hydrogen in Etch Rate Anisotropy and Pattern formation. We can now interpret most of our experimental results in terms of the role of hydrogen in EBIE of diamond. In the absence of H2, O2-mediated EBIE of diamond is isotropic. The introduction of hydrogen stabilizes the {110}
With pure O\textsubscript{2} as the precursor gas, the plasma eliminates the effect of residual water on EBIE. In the absence of the plasma, {110} basis patterns characteristic of O\textsubscript{2} EBIE affected by residual water are observed (a). With the plasma we observe the “sponge-like” texture that is characteristic of O\textsubscript{2} EBIE under anhydrous conditions (b). (c, d) Remote plasma radicalizes precursor gases in the chamber. This dramatically increases the reactivity of H\textsubscript{2} resulting in {111} and {110} basis patterns without (c) and with (d) the plasma, respectively. Scale bars in main images are 200 and 50 nm in insets. All inset images are at the same scale.

To address the question of why hydrogen modulates the etch rate in the plane-dependent manner observed in our experiments, we use DFT to calculate the adsorption energies, $E_a$ of H and O species on diamond:

$$E_a = \frac{1}{N}[E_{\text{Surf}+\text{Mol}} - (E_{\text{Surf}} + E_{\text{Mol}})]$$

where $E_{\text{Surf}+\text{Mol}}$, $E_{\text{Surf}}$, and $E_{\text{Mol}}$ are the energies of the molecule-surface system, the surface, and the adsorbing molecule (in the gas phase), respectively, and $N$ is the number of molecules adsorbed per supercell.

Table 1 lists the results of $E_a$ calculations for O, O\textsubscript{2}, H, OH, and N species upon pristine and fully terminated (1 ML) {111}, {110}, and {100} surfaces of diamond. For adsorption of oxygen upon {110} and {100} surfaces, we consider two possible configurations: ketone and ether. O bonds to a single C atom in the ketone configuration and two atoms in the ether arrangement (see SI Figure 7). Oxygen adsorbs favorably in the ketone configuration on {111} and {110} surfaces, while ether is favorable on {100}. A detailed analysis of adsorption geometries is provided in the SI. Bond distances calculated here agree well with previously reported values calculated using the DFT-GGA approximation, confirming the accuracy of our calculations. Results from simulations of both pristine and fully covered (1 ML) surfaces are presented in order to illustrate the effects of adsorbate-adsorbate interactions. However, the 1 ML results are most appropriate for direct comparison with our EBIE experiments as dangling bonds are not stable in the presence of gases which can be adsorbed.

The most important implications of these calculations are found in the comparison of O and H adsorption energies upon fully terminated surfaces. These values are highlighted in Table 1. Hydrogen adsorption can result only in bonding to a single C, the adsorption energy ($E_a^{\text{H}}$) is similar in magnitude upon all three diamond surfaces and is high relative to that of oxygen. Conversely, the oxygen adsorption energy ($E_a^{\text{O}}$) varies significantly between crystal planes. This implies that competitive adsorption of H and O will yield a different ratio of H:O coverage on each of the considered crystal planes (since the adsorbate residence time $\tau$ scales exponentially with $E_a$ according to $\propto e^{-E_a/RT}$, where $T$ is temperature). The absolute value of the difference ($|E_a^{\text{H}} - E_a^{\text{O}}|$) and ratio ($E_a^{\text{H}}/E_a^{\text{O}}$) between the hydrogen and oxygen adsorption energies for the three planes are presented in Figure 6a. Both of these values increase in the order of {100}, {111}, {110}. As a result, we expect that during EBIE performed using a mixture of hydrogen and oxygen and a low-power remote plasma during EBIE, {110} basis patterns characteristic of O\textsubscript{2} EBIE under anhydrous conditions are observed.
adsorption geometries are the most stable con
ether on {100} and ketone on {110} indicate that these
diamond surfaces considered. The high adsorption energies for
experiments performed as a function of H2:O2 partial pressure.
and correlates with the anisotropic etch rates observed in EBIE
O2 adsorption onto pristine diamond surfaces (non-highlighted
from diamond during oxygen-mediated EBIE. Simulations of
identify the most likely etch reaction product that is desorbing
and {110} planes.
and that the observed etch rate anisotropy is caused by
observation that the H2-mediated EBIE pathway is far less
efficient (Figure 2h) than the O2-mediated pathway (Figure 2a)
and that the observed etch rate anisotropy is caused by corresponding variations in H coverage of the {100}, {111}, and {110} planes.

**Etch Reaction Products.** Next, we use DFT calculations to identify the most likely etch reaction product that is desorbing from diamond during oxygen-mediated EBIE. Simulations of O2 adsorption onto pristine diamond surfaces (non-highlighted values in Table 1) indicate that, after geometry optimization, dissociative adsorption of O2 into the C=O (ketone) or C–
O–C (ether) configuration is energetically favorable over O–
C–O formation (molecular adsorption, O2) on all of the diamond surfaces considered. The high adsorption energies for ether on {100} and ketone on {110} indicate that these adsorption geometries are the most stable configurations for O on the respective planes. Following geometry optimization, no
stable ether configuration could be found upon the {111} plane (see SI Figures 7–9) and attempted molecular adsorption of O2 upon {111} resulted in two adjacent ketone groups with approximately equal adsorption energies ((111)-O vs (111)-O2 in Table 1). This indicates that ketone adsorption is strongly favored upon the {111} plane.55

Formation of stable O–C–O groups is therefore unlikely, and diamond surfaces with an O:C ratio higher than 1 are energetically unfavorable and thus unstable. CO is therefore the most likely etch product leaving the diamond surface during EBIE, since the formation of a stable etch product upon the surface is a prerequisite to electron stimulated desorption. The desorption of CO is attributed to an electron stimulated (bond scission) process since the EBIE rates of diamond are approximately independent of temperature (see ref 36 and SI Figure 1).

We note that N2 adsorption energies in Table 1 are either positive or very low (the simulations were done using pristine diamond surfaces only since they show no significant interaction between isolated N and diamond, and the same is therefore expected for the case of monolayer N coverage). This implies that stable N-terminated sites will not form and a nitrogen-mediated etch pathway should not exist. This is consistent with our experimental observations and our claim that prior reports of the EBIE of diamond using N2 as the precursor gas are in fact an artifact of residual H2O.

**Etch Rate Efficiency.** We now turn to the question of why oxygen-mediated EBIE is more efficient than hydrogen-mediated EBIE. We used DFT to calculate desorption energies, \( E_d \) corresponding to the desorption of a number of C-containing surface species from pristine and terminated diamond using

\[
E_d = (E_{\text{Surf-Vac}} + E_{\text{Atom}}) - E_{\text{Surf}}
\]

where \( E_{\text{Surf-Vac}} \) is the surface energy upon vacancy formation, and \( E_{\text{Atom}} \) and \( E_{\text{Surf}} \) are the energies of the surface and the desorbed species, respectively. Table 2 shows the results for a range of species on the {100}, {111}, and {110} surfaces. \( V_{\text{CO}} \) and \( V_{\text{CH}} \) indicate desorption of CO and CH, respectively, leaving a surface carbon vacancy.

The desorption energy for CO is far lower than for CH on all considered pristine diamond planes (top row of Table 2),

![Figure 6](image)

**Table 2. Desorption Energies, \( E_d \) (eV), for {100}, {111}, and {110} Surfaces**

<table>
<thead>
<tr>
<th>Defect</th>
<th>{100}</th>
<th>{111}</th>
<th>{110}</th>
</tr>
</thead>
<tbody>
<tr>
<td>( V_{\text{CO}} )</td>
<td>6.08</td>
<td>2.81</td>
<td>4.81</td>
</tr>
<tr>
<td>( V_{\text{CH}} )</td>
<td>11.57</td>
<td>10.16</td>
<td>10.86</td>
</tr>
<tr>
<td>( Ht-V_{\text{O}} )</td>
<td>2.48</td>
<td>2.56</td>
<td>1.12</td>
</tr>
<tr>
<td>( Ht-V_{\text{H}} )</td>
<td>4.50</td>
<td>4.37</td>
<td>3.30</td>
</tr>
<tr>
<td>( Ot-V_{\text{O}} )</td>
<td>2.29</td>
<td>1.60</td>
<td>0.15</td>
</tr>
<tr>
<td>( Ot-V_{\text{H}} )</td>
<td>4.28</td>
<td>4.65</td>
<td>2.85</td>
</tr>
<tr>
<td>( Ht-V_{\text{CO}} )</td>
<td>3.55</td>
<td>5.15</td>
<td>4.06</td>
</tr>
<tr>
<td>( Ot-V_{\text{CO}} )</td>
<td>3.33</td>
<td>3.85</td>
<td>2.72</td>
</tr>
<tr>
<td>( Ot-V_{\text{CH}} )</td>
<td>10.95</td>
<td>11.85</td>
<td>11.08</td>
</tr>
<tr>
<td>( Ht-V_{\text{CH}} )</td>
<td>10.54</td>
<td>11.92</td>
<td>11.02</td>
</tr>
</tbody>
</table>

\( Ht \) and \( Ot \) denote hydrogen terminated and oxygen terminated surfaces respectively. Energies are calculated with respect to \( O \), \( CO \), and \( CH \) in the gas phase. Here, positive values indicate the energy needed to create a defect. Desorption events that give rise to etching (etch reactions) are highlighted.
indicating a fundamental role of oxygen adatoms in weakening C–C surface bonds. Conversely, a high $E_d$ for CH suggests surface stabilization upon hydrogen adsorption and strengthening of surface C–C bonds. $E_d$ for desorption of CO is low relative to that of CH from all surfaces (bottom row, Table 2). The large differences between the calculated desorption energies of CO and CH correlate with the observed differences in the etch rate obtained using pure O$_2$ and pure H$_2$ precursor gases.

Finally, we note that the $E_d$ for an etch reaction to occur (desorption of CO or CH) is higher than is required for non-etch reactions (desorption of O or H) on all surfaces. Furthermore, $E_d$ values for non-etch reactions (entries in Table 2 that are not highlighted) are all lowest for the {110} plane. These results imply a preference for non-etch reactions over etch reactions, and this preference is greatest for the {110} plane. This correlates with the slow etch rates observed for the {110} plane during EBIE performed using a mixture of H$_2$ and O$_2$. However, we must emphasize that the energies do not translate directly to cross sections for electron stimulated desorption, and small differences between the values of $E_d$ in Table 2 therefore do not necessarily directly correlate with variations in the EBIE rates of different crystal planes.

Fabrication of Large-Scale Structures by Anisotropic EBIE. Anisotropic EBIE provides control over the degree of surface roughness that is needed for applications that require control over surface area and related functional properties such as wettability. However, as we show below, the etch rate anisotropy can also be used to fabricate large-scale structures defined by the symmetry of the diamond crystal lattice and surfaces that appear very smooth in SEM and AFM images.

If EBIE is continued for extended periods under anisotropic etch conditions, inverse pyramid-like structures evolve during subsequent anisotropic EBIE of the region. A similar anisotropic etch process was performed on individual circular holes etched under isotropic conditions (b). (g) A structure formed from a circular hole after 40 min of anisotropic EBIE of the surrounding region. (h, i) Evolution of a separate circular hole, shown here after 30 h and 60 (i) min of anisotropic EBIE. The typical evolution observed involves formation of both {111} and {110} planes with the {111} planes receding and roughening, while large, smooth {110} plane sidewalls form as EBIE is continued. (j–l) Circular silica disks made with electron beam lithography can act as an electron blocking mask and allow fabrication of pillars. Anisotropic conditions yield a faceted pillar (j, k). The inset shows the silica disk atop the pillar shown in (j). The faceted pillar top can be seen through the circular outline of the mask. (l) Under isotropic conditions, a smooth cylindrical pillar is obtained. All scale bars are 200 nm except for in (b–d) and (j) which are 1 μm. The {100} crystal directions indicated in (b) apply to all images. The images in (j–l) were taken at 45, 35, and 30° tilt, respectively.
respectively. The holes initially evolve into structures with smooth \{111\} planes at the top and smooth \{110\} planes below with a rough etch pit base. As etching is continued, the \{111\} planes recede, and the \{110\} planes grow. In a similar experiment, anisotropic EBIE was performed on individual circular holes. Figure 7g–i shows representative examples of typical structures observed at different stages of anisotropic etching. Both \{111\} and \{110\} planes initially form, with the \{111\} features diminishing and \{110\} planes expanding as etching is continued. AFM was used to image similar pits (see SI Figure 5). The inclination of the smooth sidewalls was measured from these images to be $-45 \pm 3^\circ$ with respect to the \{110\} plane, confirming that they are \{110\} planes.

We also used electron beam lithography to fabricate circular silica disks to act as electron blocking masks during EBIE. Under highly anisotropic etch conditions, we obtain a faceted pillar with a very smooth surface. An example is shown in Figure 7j,k. Note the inset showing a top-down view of the pillar. The faceted pillar top can be seen through the circular outline of the silica mask, highlighting how the pillar geometry is determined by both the anisotropic etch kinetics and the mask geometry. Using isotropic etch conditions, we obtain cylindrical pillars (Figure 7l) with more undercutting of the silica etch mask.

These demonstrations illustrate the potential of EBIE for deterministic top-down nanofabrication in single-crystal diamond. Using isotropic EBIE it is possible to etch structures with arbitrary geometries at a maximized rate (see SI Figure 4). Conversely, anisotropic EBIE can be utilized to obtain large and smooth \{110\} planes that could be exploited for the fabrication of structures such as pyramids and V-grooves in \{100\} plane diamond.

**CONCLUSIONS**

We performed a detailed study of the EBIE kinetics of diamond and delineated the roles of oxygen and hydrogen species. We found that EBIE of single crystal diamond results in isotropic etching using O$_2$ as the precursor gas under anhydrous conditions and that the most likely etch reaction product leaving the diamond surface is CO. Addition of H$_2$ to the O$_2$ precursor gas selectively inhibits the etch rate of different crystal planes and makes etching anisotropic. The anisotropy gives rise to the formation of topographic surface patterns with symmetries defined by that of the crystal lattice and is attributed to preferential coverage of specific crystal planes by hydrogen. The coverage variations are a consequence of competitive adsorption of O and H and large differences in the adsorption energy of O on different crystal planes. The reduction in the etch rate caused by hydrogen is attributed to weakening of C–C surface bonds by O adsorbrates and stabilization of the bonds by H. Our results constitute the first detailed description of anisotropic EBIE rate kinetics. In practice, the anisotropy can be controlled by varying the O$_2$ to H$_2$ partial pressure ratio and by radicalizing the precursor gas using a remote RF plasma generator. More broadly, the remote plasma can also be used to suppress undesired effects of residual H$_2$O molecules and to activate chemically stable gases and enable their use as precursors for electron stimulated surface processing. Isotropic EBIE with pure O$_2$ is capable of high-rate localized etching of diamond with nanostructure geometry dictated only by the electron beam scan pattern and/or mask used. Anisotropic EBIE using a H$_2$/O$_2$ mix can be used to fabricate structures with large and smooth \{110\} crystal planes in single crystal diamond.

**METHODS**

*Sample Preparation.* The samples used in this study were boron-doped \{100\} plane, CVD grown, type 2a, single crystal diamonds, polished on both sides and purchased from Microwave Enterprises, Ltd. Extensive cleaning was found to be necessary for reproducibility and was performed prior to all experiments. Sequential ultrasonication in acetone, IPA, hexane, chloroform, ethanol, and ultrapure deionized water was first performed for 30 min each. Immersion in boiling piranha solution (3:1 mixture of 96% H$_2$SO$_4$:30% H$_2$O$_2$) at 155 °C with periodic replenishment of H$_2$O$_2$ was then performed for 30 min. This was followed by rinsing with DI water, a second piranha solution immersion with ultrasonication at room temperature, ultrasonication with ultrapure water, and finally drying in a stream of N$_2$. Samples were immediately loaded into the SEM chamber after cleaning and subject to overnight plasma cleaning with oxygen gas using a low-power remote plasma decontaminator system (EVACTRON model C from XEI scientific). The O$_2$ plasma cleaning further removes carbonaceous contaminants and lowers residual water concentration.

*Electron Beam-Induced Etching of SC Diamond.* EBIE was performed using a customized FEI Sirion field emission gun SEM, outfitted for variable-pressure operation. A homemade gas delivery system enables precursor input with high-precision flow control. Precursors used were high-purity hydrogen, oxygen, nitrogen, and Ar (all $\geq$99.99%), obtained from Sigma-Aldrich as well as ultrapure deionized water. Gas input lines pass through a cold trap, held at 116 K for precursors other than H$_2$O. All gas lines were extensively flushed with dry N$_2$ prior to experiments.

Unless noted otherwise, all EBIE experiments, apart from those shown in Figure 7, were performed at room temperature using a 1.5 keV, 9.5 nA electron beam, scanned in a raster pattern to expose a 2.9 × 2.0 μm region of the sample surface to an average electron flux of 1.5 × 10$^{10}$ e$^-\mu$m$^2\cdot$s$^{-1}$. The raster consisted of 484 lines per frame, 30 nm pitch between lines, and 1.68 μm line time. An analog sine wave voltage signal was connected to the horizontal scan coil (direction) and was therefore not discretized to individual dwell points. Each irradiation was performed for 20 min except the pits shown in Figure 4e–g, which were etched for 40 min. A pressure of approximately 9 Pa was used for all EBIE experiments utilizing a single precursor. For the experiments involving H$_2$ and O$_2$ mixing, the total chamber pressure was 9 ± 1.5 Pa. The pit shown in Figure 2g was an exception, and a total pressure of 12.6 Pa was used. The same remote plasma unit used for chamber decontamination (EVACTRON model C) was active during EBIE for all etch pits shown in Figure 2 and others where specified. An RF power of 5 W at 13.56 MHz was used for all plasma active experiments, chamber cleaning, and residual water suppression.

In Figure 7a, the inverse pyramid shown formed during EBIE of a 6.0 × 4.14 μm region with the same beam parameters described above and a H$_2$O$_2$ ratio of 0.78. In Figure 7, approximately circular holes were etched with a 3 keV, 0.17 nA, stationary focused beam, and a 40 s total dwell time. Anisotropic EBIE was performed with a 1.5 keV beam scanned in a digitized raster pattern consisting of a square matrix of 10$^4$ pixels with 10 μs pixel dwell time. The etch frames and beam currents used were 18.5 × 18.5 μm, 21 nA for the array (Figure 7c–f), and 3.5 × 3.5 μm, 5.6 nA for individual etches (Figure 7g–i), resulting in electron fluxes of 3.81 × 10$^3$ and 2.85 × 10$^3$ e$^-\mu$m$^2\cdot$s$^{-1}$, respectively. A H$_2$:O$_2$ ratio of 0 and 2.2 with 10 Pa total chamber pressure was used for isotropic and anisotropic EBIE steps, respectively. Plasma was active during all steps. Silica disks of ~200 nm thickness were deposited by electron beam lithography using the negative resist hydroquinone silesquioxane (HSQ). EBIE of pillars was then performed using a 1.5 keV, 21 nA beam with the same raster pattern used for the pits of Figure 2, to expose a 4 × 2.7 μm region with the disk centered in the frame. Etch times were 4 and 1 h for the pillars shown in (j–k) and (l), respectively.

*DFT Computational Method.* The calculations presented in this work were performed using a DFT approach, within the generalized
gradient approximation (GGA) using the Perdew–Burke–Emzerhof (PBE) functional for the exchange–correlation term.\textsuperscript{56} We use periodic boundary conditions and localized atomic orbital basis set as implemented in SIESTA code, where the core–valence interaction is described by the norm conserving pseudopotential.\textsuperscript{59,60} Double-$\zeta$ plus polarization orbitals (DZP) were applied, and the cutoff energy for the valence electrons was set to 750 $\text{Ry.}$\textsuperscript{60,61} $\Gamma$ point calculations have been used for a $(6 \times 6), (6 \times 4),$ and $(4 \times 4)$ expansion of the $(111), (110),$ and reconstructed $(100)$ surfaces, consisting of 12 atomic layers, with a vacuum gap of ca. 25 $\text{Å.}$ Full geometry optimization has been carried out for each system, and the convergence criteria for the energy and forces are $10^{-4}$ eV and $10^{-2}$ eV/$\text{Å},$ respectively.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.8b00354. Data and discussion concerning EBIE at elevated temperature, electron flux dependency, control experiments with inert gases as well as AFM and quantitative etch rate data is included. There are also further DFT calculations including bond lengths, surface formation energies, $E_a$ and $E_g$ for species other than O and H, and schematics illustrating adsorption geometries (PDF)

**AUTHOR INFORMATION**

*Corresponding Author*

*E-mail: James.Bishop@student.uts.edu.au*

**ORCID**

James Bishop: 0000-0001-6895-7544

Igor Aharonovich: 0000-0003-4304-3935

Milos Toth: 0000-0003-1564-4899

**Author Contributions**

$^*$These authors contributed equally to this work.

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors gratefully acknowledge funding from the Australian Research Council (project nos. DP140102721 and DP160101301), the National Natural Science Foundation of China (no. S1323011), the Asian Office of Aerospace Research and Development grant (FA2386-17-1-0406), and the Office of Naval Research Global (N62909-18-1-2025). The theoretical calculations in this research were undertaken with the assistance of resources from the National Computational Infrastructure (NCI), which is supported by the Australian Government.

**REFERENCES**


