

# Deterministic Nanopatterning of Diamond Using Electron Beams

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**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 nano-scale using oxidizing precursor gases such as O<sub>2</sub> and H<sub>2</sub>O. Here we explain the roles of oxygen and hydrogen in the etch process and show that oxygen gives rise to rapid, isotropic etching, whilst 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 micro-structures 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,<sup>1–3</sup> non-linear optics,<sup>4,5</sup> microelectromechanical systems (MEMS),<sup>6</sup> acoustic devices,<sup>7</sup> and electrochemistry.<sup>8</sup> It also holds promise for improving the performance of more conventional electronic devices.<sup>9–11</sup> 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.<sup>12–16</sup>

For many of those applications, controlling the diamond surface is of paramount importance. For example, induc-

ing controlled patterning to expedite neuron growth on diamond surfaces has been a long standing goal in exploiting diamond in bio-sensing applications.<sup>17</sup> For photonic applications, enhancing light extraction by ameliorating the diamond surface *via* direct patterning of cones can also be advantageous.<sup>18,19</sup> Exposing particular surfaces (e.g. {111} over {100} planes) can be a viable method to enhance incorporation of color centers.<sup>20</sup> Finally, emerging applications of diamond in electrochemistry and catalysis are only in their infancy,<sup>21,22</sup> and morphology control by direct surface patterning can be highly beneficial to improve final device performance.

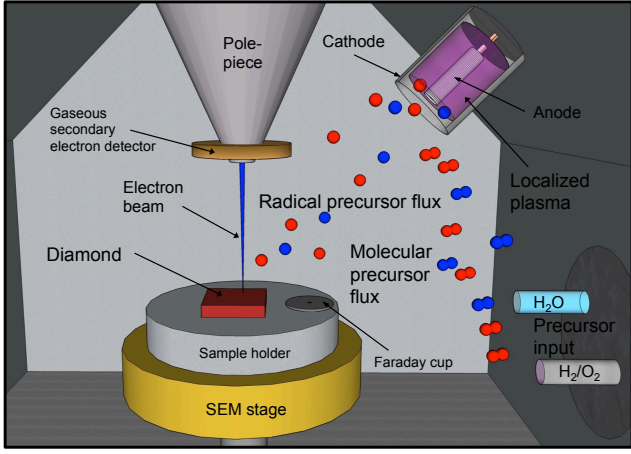
Electron beam induced etching (EBIE)<sup>23–26</sup> has recently emerged as a versatile technique that can be used to etch diamond with no damage detected by Raman and photoluminescence spectroscopy.<sup>19</sup> The technique is capable of single step, beam-directed chemical etching of a broad range of materials<sup>27–30</sup> with high spatial resolution ( $\sim 10$  nm).<sup>31,32</sup> 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 O<sub>2</sub> or H<sub>2</sub>O precursor gases, and most studies of EBIE report etching that is isotropic.<sup>33–35</sup> However, we recently demonstrated that H<sub>2</sub>O EBIE of single crystal diamond is anisotropic and as a result, yields nanostructured topographic surface patterns.<sup>36</sup> 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 use of O<sub>2</sub> as the precursor gas gives rise to high-rate, isotropic etching of single crystal diamond, while the addition of H<sub>2</sub> reduces the etch rate and makes it anisotropic due to preferential passivation of specific crystal planes (i.e. hydrogen alters the etch selectivity of certain crystal planes over others). We elucidate the diamond volatilization mechanism and show that the anisotropy and the geometries of the resulting surface structures can be controlled over a broad range of length scales by the partial pressure of hydrogen and by using a remote RF plasma source to radicalize the precursor gas. The work also shows that residual H<sub>2</sub>O contaminants play a critical role in etch rate anisotropy, and that these undesired side-effects can be suppressed us-

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**Figure 1.** Schematic of the experimental apparatus used for EBIE. The field emission gun SEM is outfitted for variable pressure operation and an external gas delivery system enables precise metering and delivery of the gases  $O_2$ ,  $H_2$ , Ar,  $N_2$  and  $H_2O$ .  $H_2O$  is delivered *via* a dedicated line to avoid contamination of other gases. An *in-situ* RF remote plasma generator serves a dual purpose. It is used prior to EBIE with  $O_2$  gas to reduce the concentration of residual organic and water contaminants, and during EBIE to radicalize precursor gases and increase their reactivity.

ing a remote RF plasma source. Our results increase present understanding of electron-surface interactions and are important for the design and control of electron stimulated nanofabrication processes.

## Results and discussion

A schematic depicting the experimental setup used for EBIE is shown in figure 1. In order to determine the roles of hydrogen and oxygen species in etching of diamond, we performed experiments using high purity  $H_2$ ,  $O_2$ ,  $H_2O$  and mixtures of these gases as the etch precursors. It must first be noted that highly controlled environments are essential for reproducible EBIE. Organic contaminants must be removed from samples prior to EBIE and the necessary sample preparation procedures are detailed in the Methods section and Supporting Information (SI). It must also be noted that residual  $H_2O$  is abundant in the high vacuum systems normally used for EBIE, and it gives rise to electron induced oxidation and etching of carbonaceous materials.<sup>37–39</sup> Active suppression of residual  $H_2O$  was found to be the second necessary prerequisite for the present study, and we discovered that the use of a low power RF remote plasma generator can not only eliminate the effects of organic contaminants,<sup>40,41</sup> but also those of residual water. It can therefore enable robust electron stimulated processing of surfaces, as is detailed below.

Figure 2 shows a set of etch pits fabricated by EBIE in  $\{100\}$ -oriented, B-doped, CVD grown, type 2a single crystal (SC) diamond using  $H_2$  and  $O_2$  precursor gases. All results presented in this work were obtained at room temperature (RT), except for figure 1 of the Supporting Information (SI). Each etch pit was made by scanning the electron beam in a rectangular raster pattern.  $R_p$  designates the ratio of the  $H_2$  to the  $O_2$  partial pressure, which was varied from pure  $O_2$  (fig. 2(a)) to a value of 8.6 (fig. 2(g)) by controlling the flow rates of the individual precursor gases. In addition, figure 2(h) and (i) show etch pits fabricated using pure  $H_2$  and pure  $H_2O$ , respectively. The latter is included here for

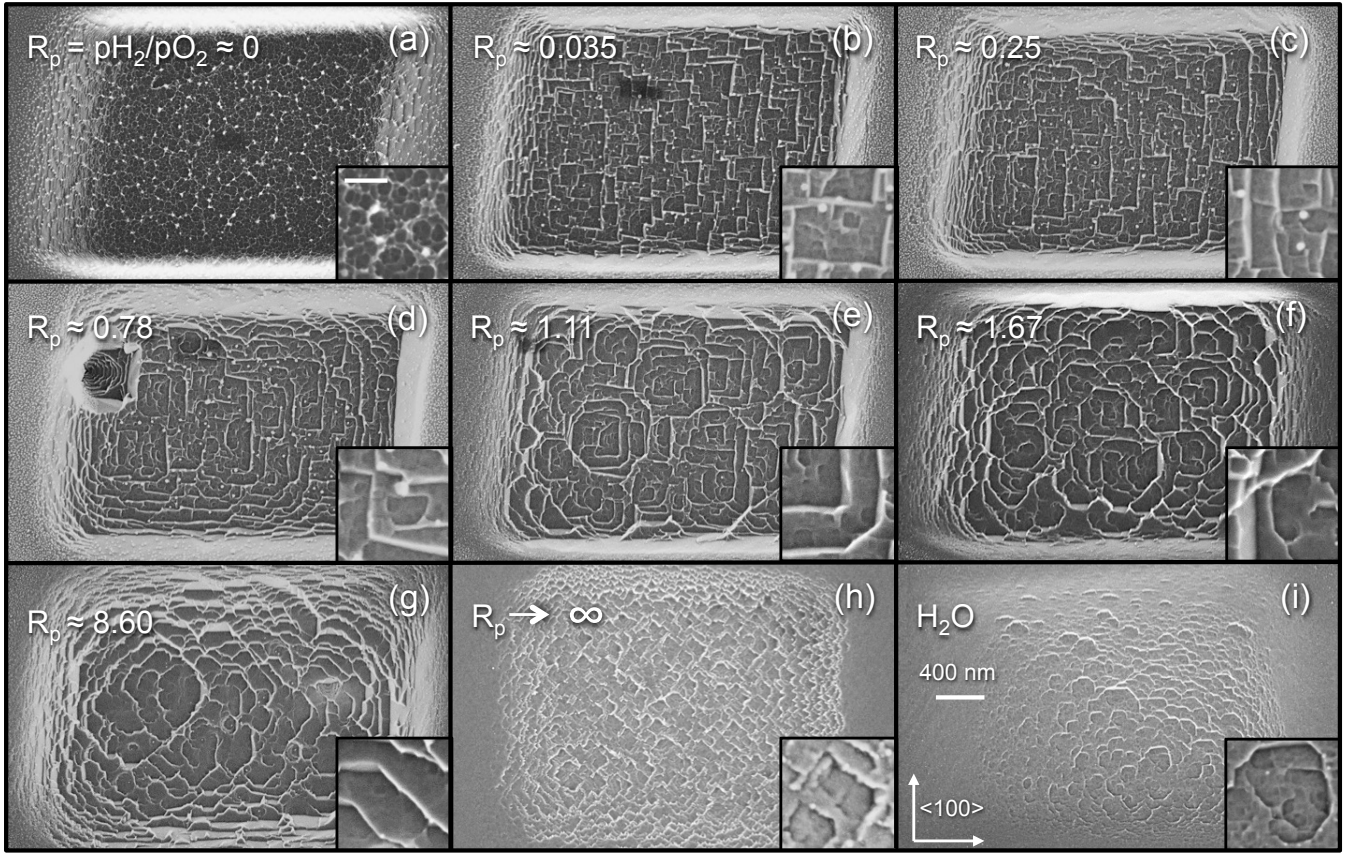
reference and shows the topographic patterns reported in our prior work on  $H_2O$  EBIE of diamond.<sup>36</sup>

Using pure  $O_2$  ( $R_p \approx 0$ ), we observe a ‘sponge-like’ surface texture at the etch pit base (fig. 2(a)) and the morphological features are not aligned with crystallographic directions. The lack of pattern formation shows that  $O_2$  EBIE gives rise to isotropic etching of diamond. As hydrogen is added to the system (increasing  $R_p$  in fig. 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 (ie. selectivity) of different crystal planes. The etch frames are aligned with the edge of the diamond prior to EBIE<sup>36</sup> such that all etch pit sidewalls are approximately parallel to  $\langle 100 \rangle$  directions. At low  $R_p$  values (corresponding to small amounts of  $H_2$ ) we observe square and rectangular patterns (fig. 2(b - c)) which evolve towards octagonal patterns at elevated  $R_p$  values (fig. 2(d - g)). In pure  $H_2$  ( $R_p \rightarrow \infty$ ), the pattern edges are aligned at  $45^\circ$  with respect to  $\langle 100 \rangle$  crystal directions (fig. 2(h)).

Electron irradiation of diamond in the presence of the inert gases  $N_2$  and Ar did not give rise to etching (see SI fig. 3), and we attribute prior reports of EBIE by these gases<sup>42,43</sup> to the effects of residual  $H_2O$  demonstrated previously.<sup>37</sup> Whilst pure  $H_2$  gives rise to etching of diamond, the etch rate is very low compared to that of  $O_2$  EBIE (under equivalent conditions), indicating that the etch pathway is significantly less efficient. We obtained an etch rate of  $0.32 \mu m^3/min$  for  $O_2$  and  $0.06 \mu m^3/min$  for  $H_2$  (see SI fig. 4), under our experimental conditions (detailed in Methods). Using  $H_2O$  as precursor (fig. 2(i)), octagonal patterns form similar to those fabricated using a mixture of  $H_2$  and  $O_2$  at  $R_p = 1.67$ . However, the etch rate is significantly lower with  $H_2O$  than with  $O_2$  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).<sup>36</sup> 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<sup>44,45</sup> 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.<sup>46</sup>

A crystallographic analysis of the patterns formed in the etch pits of figure 2 is presented in figure 3. Using pure  $O_2$ , no patterns are observed and etching is isotropic, whilst the addition of hydrogen gives rise to the formation of planes of the  $\{110\}$  family. We refer to these patterns as  $\{110\}$  basis. As  $R_p$  is increased, planes of the  $\{111\}$  family are partially formed with edges aligned with  $\langle 110 \rangle$  directions ( $45^\circ$  to  $\langle 100 \rangle$  directions). This results in the octagonal patterns observed at higher  $R_p$ . We refer to these patterns as ‘ $\{110\} + \{111\}$ ’ basis. It must be noted that whilst smooth  $\{110\}$  planes do form,  $\{111\}$  planes always appear rough and partly etched. As  $R_p$  is increased further towards infinity,  $\{111\}$  planes contribute increasingly to the patterns. Using pure  $H_2$ , the majority of edges in the patterns are aligned with  $\langle 110 \rangle$  directions and formed by  $\{111\}$  planes. We refer to these patterns as  $\{111\}$  basis. However, even with pure  $H_2$ , large smooth  $\{111\}$  planes do not form.



**Figure 2.** EBIE of  $\{100\}$  plane SC diamond using different ratios of  $\text{H}_2$  and  $\text{O}_2$  precursor gases. A remote plasma was used during EBIE for precursor radicalization and residual water reduction. The partial pressure ratio of hydrogen to oxygen ( $R_p$ ) used for each etch is indicated. Insets (all at the same scale, scale bar = 100 nm) show close-ups of key surface morphologies. We observe a “sponge-like” texture and lack of patterns with pure  $\text{O}_2$  indicating an isotropic etch (a). As  $R_p$  is increased we see rectangular  $\{110\}$  basis patterns (b - c), and increasing contributions from  $\{111\}$  planes (d - g), resulting in octagonal patterns. Pure  $\text{H}_2$  results in  $\{111\}$  basis patterns (h). EBIE with  $\text{H}_2\text{O}$  also gives rise to octagonal patterns (i). Etch times and conditions were equal for all pits. The pit depths are 894 (a), 460 (b), 530 (c), 552 (d), 450 (e), 451 (f), 545 (g), 157 (h) and 258 nm (i) respectively. The etch rate with  $\text{H}_2\text{O}$  or  $\text{H}_2$  is lower than with  $\text{O}_2$  or  $\text{O}_2 + \text{H}_2$ . The etch pit sidewalls are aligned with the substrate edges and therefore  $\langle 100 \rangle$  crystal directions which are indicated in (i) and apply to all images. Edges aligned with pit sidewalls are formed by  $\{110\}$  planes and those at  $45^\circ$  by  $\{111\}$  planes. All main images are at the same scale indicated by the scale bar in (i).

## Role of a remote plasma in EBIE of diamond

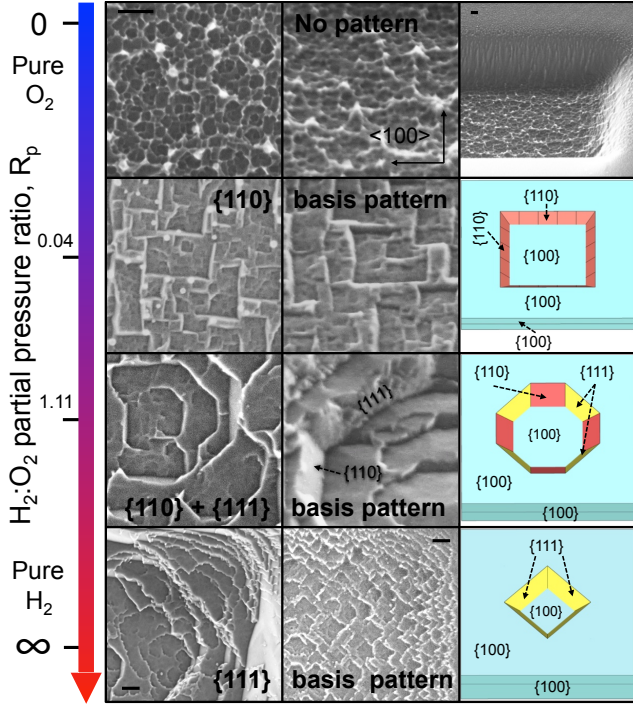
In this section we elucidate the roles of a remote plasma on EBIE performed using  $\text{O}_2$ ,  $\text{H}_2$  and  $\text{H}_2\text{O}$  precursor gases, and on residual  $\text{H}_2\text{O}$  contaminants. The patterns discussed up to this point were fabricated by EBIE performed in the presence of 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 pre-condition 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 ( $R_p \approx 0$ , fig. 4(a)), 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  $R_p \approx 0.26$  (fig. 4(b)), which is a condition at which  $\{110\}$  basis patterns are observed in the presence of a remote plasma (fig. 2(b)).

At higher hydrogen partial pressures,  $\{110\}$  basis patterns

do occur even in the absence of a plasma, but we observe no  $\{111\}$  contributions to the patterns even with pure  $\text{H}_2$  (compare fig. 2(f) and 2(h)). 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 fig. 2(i) and fig. 4(g)), as is the case for pure  $\text{O}_2$  (see fig. 2(a) and fig. 4(a)). 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  $\text{H}_2\text{O}$  in the experiments. Very slow etching is observed, seen as roughening of the diamond surface (fig. 4(h)), consistent with etching mediated by low levels of residual  $\text{H}_2\text{O}$ . High magnification images of the surface reveal patterns similar to those produced when  $\text{H}_2\text{O}$  is used intentionally as an etch precursor gas, albeit on a smaller scale. The high vacuum irradiation (fig. 4(h)) was performed after  $\text{H}_2$  EBIE (fig. 4(f)) and prior to the intentional introduction of  $\text{H}_2\text{O}$  (fig. 4(g)), confirming that the surface morphology generated by pure  $\text{H}_2$  seen



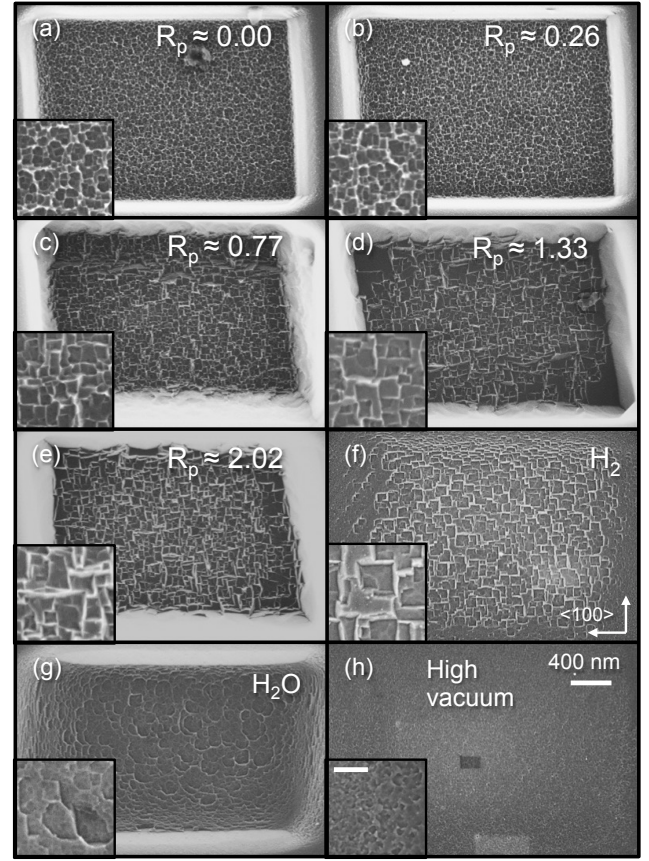
**Figure 3.** High magnification SEM images of the topographical patterns formed using different ratios of  $H_2:O_2$  ( $R_p$ ) for EBIE of  $\{100\}$  plane diamond. Idealized geometrical figures are shown at right to aid visualization of features which comprise the patterns. With pure  $O_2$  (top row), we obtain isotropic etching and no patterns.  $\{110\}$  planes form at low  $R_p$  (second row) and result in rectangular patterns. At high  $R_p$  (fourth row),  $\{111\}$  planes primarily dictate the patterns, forming edges aligned at  $45^\circ$  to  $\langle 100 \rangle$  directions. At intermediate  $R_p$  (third row) we observe octagonal patterns composed of smooth  $\{110\}$  planes and rough  $\{111\}$  planes. Even with pure  $H_2$ , smooth  $\{111\}$  planes do not form and clearly still etch faster than  $\{110\}$  planes yet slower than  $\{100\}$  planes. Diamond shaped features are formed yet the geometrical ideal of an etch pit composed entirely of  $\{111\}$  planes is never fully realized. Images in the second column apart from the bottom image were taken at  $45^\circ$  tilt. Scale bars are 100 nm, Images are at the same scale as top left unless a separate scale bar is provided.

in figure 4(f) is not an artifact of residual  $H_2O$ .

Finally, we show directly that the above effects of residual  $H_2O$  can affect  $O_2$  EBIE and  $H_2$  EBIE, and that the effects of  $H_2O$  contaminants can be suppressed by igniting a remote plasma either before or during etching. We start with  $O_2$  and, critically, in this experiment we did not ignite the plasma before we performed  $O_2$  EBIE (in contrast to the experiment shown in fig. 4).  $\{110\}$  basis patterns are observed during  $O_2$  EBIE (fig. 5(a)), which are indicative of etch kinetics that are affected by residual  $H_2O$  (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 (fig. 5(b)) that is characteristic of  $O_2$ -mediated EBIE under anhydrous conditions (see fig. 2(a)). The same etch morphology was observed for several hours after the plasma was extinguished, demonstrating that an  $O_2$  plasma can be used prior to etching to temporarily suppress the effects of residual water.

The experiment was then repeated with  $H_2$  precursor gas, showing that  $\{110\}$  and  $\{111\}$  basis patterns are observed in the absence (fig. 5(c)) and the presence (fig. 5(d)) of

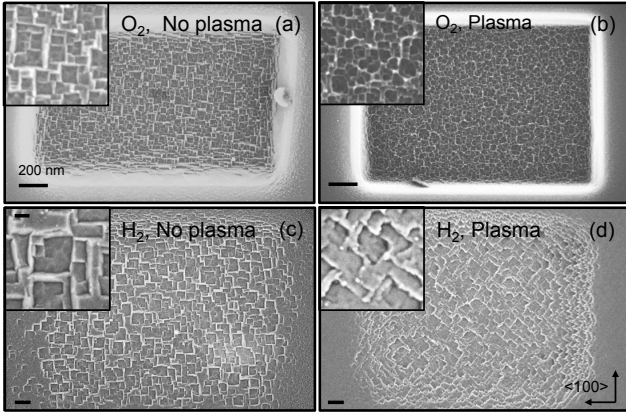


**Figure 4.** EBIE without plasma. (a - f): EBIE pits made with different  $H_2:O_2$  partial pressure ratios ( $R_p$ ), without the utilization of a remote plasma for precursor radicalization. Anhydrous conditions were achieved by  $O_2$  plasma cleaning prior to EBIE but plasma was inactive during EBIE. Adding  $H_2$  to the system has a lesser effect on EBIE kinetics compared to when a plasma is employed. Only  $\{110\}$  basis patterns are observed even with  $R_p \rightarrow \infty$ . (g - h): A control irradiation was performed in high vacuum following EBIE with  $H_2$  to confirm that residual water levels remained negligible throughout. High magnification images reveal ‘proto-patterns’ similar to those observed using  $H_2O$  as the precursor gas. Patterns formed during EBIE with  $H_2O$  are unaffected by the presence or absence of plasma. All main images are at the same scale indicated by the scale bar in (h). Insets are at the same scale (scale bar = 100 nm).

a remote plasma, respectively. The results confirm that the plasma increases the ability of  $H_2$  to participate in EBIE. This result demonstrates unambiguously 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  $H_2$ ,  $O_2$ -mediated EBIE of diamond is isotropic. The introduction of hydrogen stabilizes the  $\{110\}$  plane, causing the etch rate to decrease rapidly relative to that of the  $\{111\}$  and  $\{100\}$  planes, giving rise to  $\{110\}$  basis patterns. As the amount or reactivity of hydrogen is increased, we eventually observe  $\{111\}$  contributions to the patterns (fig. 2(f - g)). This implies increased stabilization of the  $\{111\}$  plane, a de-



**Figure 5.** Effects of employing a low power remote plasma during EBIE. (a - b): With pure  $O_2$  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  $O_2$  EBIE affected by residual water are observed (a). With the plasma we observe the ‘sponge-like’ texture that is characteristic of  $O_2$  EBIE under anhydrous conditions (b). (c - d): Remote plasma radicalizes precursor gases in the chamber. This dramatically increases the reactivity of  $H_2$  resulting in  $\{111\}$  and  $\{110\}$  basis patterns without (c) and with (d) the plasma, respectively. Scale bars in main images are 200 nm and 50 nm in insets. All inset images are at the same scale.

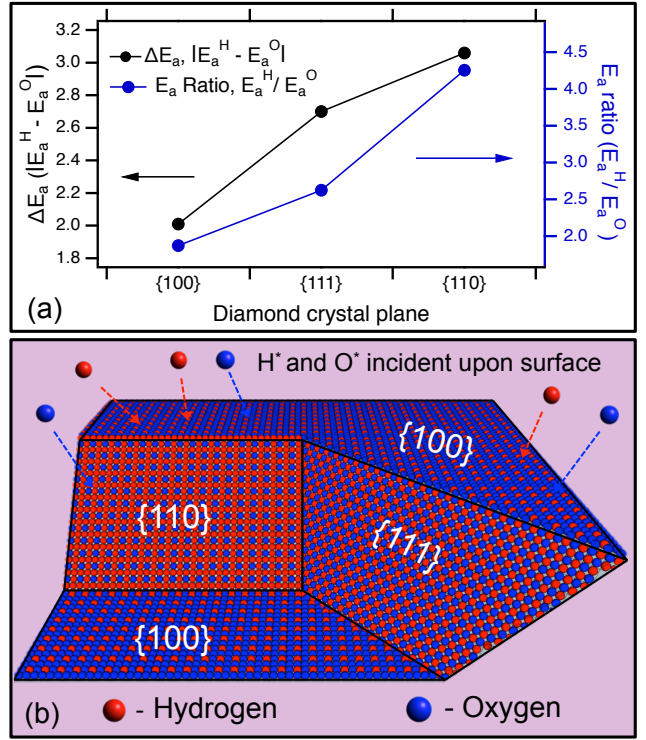
crease in the  $\{111\}$  etch rate and that both the  $\{110\}$  and  $\{111\}$  planes etch slower than  $\{100\}$  planes.  $\{111\}$  features become increasingly prominent as the amount or reactivity of hydrogen is increased further, implying an additional decrease in the  $\{111\}$  etch rate relative to the other planes. However, we do not observe smooth  $\{111\}$  planes in SEM images even when pure  $H_2$  is used as the precursor gas, indicating that the etch rate of  $\{111\}$  planes remains higher than that of  $\{110\}$  planes.

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:

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

where:  $E_{\text{Surf+Mol}}$ ,  $E_{\text{Surf}}$  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 super-cell.

Table 1 lists the results of  $E_a$  calculations for O,  $O_2$ , 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 fig. 7). Oxygen adsorbs favorably in the ketone configuration on  $\{111\}$  and  $\{110\}$  surfaces, whilst ether is favourable on  $\{100\}$ .<sup>52</sup> 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,<sup>49,53,54</sup> 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



**Figure 6.** (a): Difference ( $|E_a^H - E_a^O|$ ) and ratio ( $E_a^H/E_a^O$ ) of full monolayer (1 ML) adsorption energies for hydrogen and oxygen on the  $\{100\}$ ,  $\{111\}$  and  $\{110\}$  planes of diamond, calculated using DFT. The value is averaged over the number of atoms in the monolayer. (b): Conceptual schematic illustrating the implications of the calculated adsorption and desorption energies and the origin of anisotropic EBIE of SC diamond. When both H and O are present, we expect the adsorbed coverage ratio of H:O on the planes to increase in the order of  $\{100\}$ ,  $\{111\}$ ,  $\{110\}$ . The etch pathway for H terminated sites is far less efficient than O terminated sites making the etch rate of each plane a function of the H:O surface coverage ratio.

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 ( $E_a^H$ ) is similar in magnitude upon all three diamond surfaces and is high relative to that of oxygen. Conversely, the oxygen adsorption energy ( $E_a^O$ ) 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  $\tau \propto e^{E_a/T}$ , where  $T$  is temperature). The absolute value of the difference ( $|E_a^H - E_a^O|$ ) and ratio ( $E_a^H/E_a^O$ ) between the hydrogen and oxygen adsorption energies for the three planes are presented in figure 6(a). 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, the coverage ratio of hydrogen to oxygen on the planes will increase in the same order. This is illustrated in figure 6(b) and correlates with the anisotropic etch rates observed in EBIE experiments performed as a function of  $H_2:O_2$  partial pressure. Specifically, an increase in H coverage expected from the simulations correlates with a decrease in the observed etch rate of that plane. Hence, we conclude that hydrogen acts to inhibit the oxygen-mediated etch rate, which is

**Table 1.** Adsorption energies for O, H and N species,  $E_a$  (eV), upon the {100}, {111} and {110} planes of diamond. 1 ML denotes the adsorption energy per atom, upon a surface terminated with a monolayer of that species (highlighted). The other calculations are for a pristine, unterminated diamond surface. Energies are calculated with respect to a molecule in the gas phase, and negative values indicate attractive interactions. We also include literature values for comparison. Values sourced from literature are calculated with a range of alternative approximations and basis sets resulting in significant variation. Conclusions should be drawn only from DFT datasets calculated with the same approximations and basis sets. (Oxygen and nitrogen adsorption has also been calculated with respect to its atomic form. These values are indicated by an asterisk. The values for molecular adsorption of  $O_2$  are reported per oxygen atom.)

Adsorption energy, $E_a$ (eV)		
Surface	This Work	Other Works
{100}-H	-4.72	–
{100}-H 1ML	-4.31	-4.30 <sup>47</sup>
{100}-O(ket)	-2.83 / -6.15*	–
{100}-O(eth)	-4.17 / -7.50*	–
{100}-O 1ML (eth)	-2.30 / -5.63*	-6.21(eth)* <sup>47</sup>
{100}- $O_2$	-1.27	–
{100}-OH	-3.85	-4.13 <sup>47</sup>
{100}-N	0.02/ -4.74*	–
{111}-H	-4.37	–
{111}-H 1ML	-4.36	-4.34, -4.38 <sup>48</sup>
{111}-O	-1.96 / -5.29*	-5.57* <sup>49</sup>
{111}-O 1ML	-1.66 / -4.99*	–
{111}- $O_2$	-1.95	–
{111}-OH	-4.38	-3.43, -4.70 <sup>48,50</sup>
{111}-N	1.57/ -3.18*	–
{110}-H	-4.20	–
{110}-H 1ML	-4.00	-4.33 <sup>51</sup>
{110}-O(ket)	-3.13 / -6.46*	–
{110}-O(eth)	-1.76 / -5.09*	–
{110}-O 1ML (ket)	-0.94 / -4.27*	–
{110}- $O_2$	-2.38	–
{110}-OH	-4.50	–
{110}-N	-0.02/ -4.77*	–

consistent with our observation that the  $H_2$  mediated EBIE pathway is far less efficient (fig. 2(h)) than the  $O_2$  mediated pathway (fig. 2(a)), 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  $O_2$  adsorption onto pristine diamond surfaces (non - highlighted values in table 1) indicate that, after geometry optimisation, dissociative adsorption of  $O_2$  into the C=O (ketone) or C-O-C (ether) configuration is energetically favourable over O-C-O formation (molecular adsorption,  $O_2$ ) 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 fig. 7 - 9) and attempted molecular adsorption of  $O_2$  upon {111} resulted in two adjacent ketone groups with approximately equal adsorption energies ({111}-O vs {111}- $O_2$  in table 1). This indicates that ketone adsorption is strongly favoured upon the {111} plane.<sup>55</sup>

Formation of stable O-C-O groups is therefore unlikely and diamond surfaces with an O:C ratio higher than 1 are energetically unfavourable 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 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.<sup>36</sup> and SI fig. 1).

We note that  $N_2$  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  $N_2$  as the precursor gas are in fact an artifact of residual  $H_2O$ .

## Etch rate efficiency

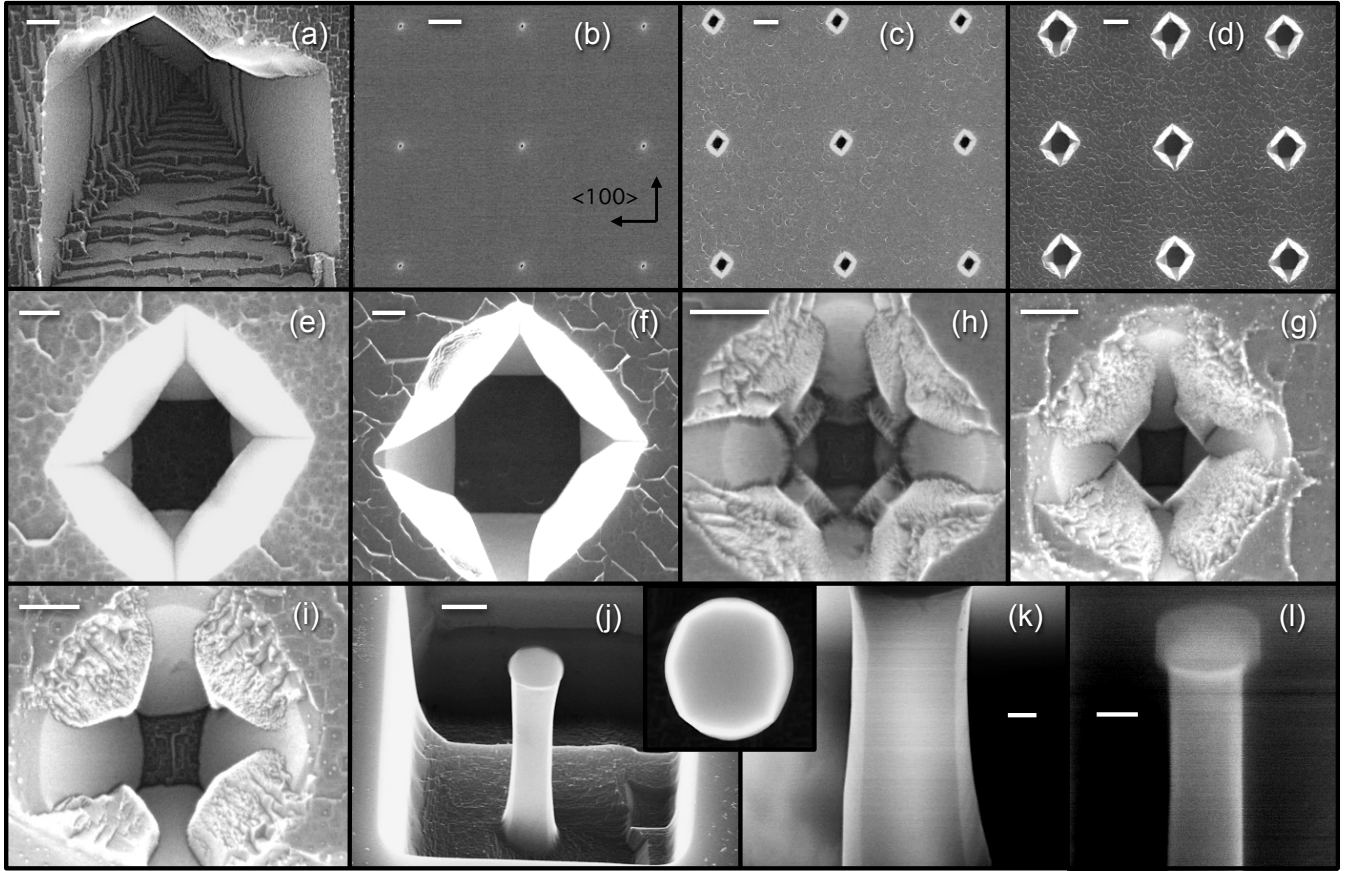
We now turn to the question of why oxygen mediated EBIE is more efficient than hydrogen mediated EBIE. We used DFT to calculate desorption energies,  $E_d$  corresponding to the desorption of a number of C-containing surface species from pristine and terminated diamond using:

$$E_d = (E_{\text{Surf-Vac}} + E_{\text{Atom}}) - E_{\text{Surf}} \quad (2)$$

Here,  $E_{\text{Surf-Vac}}$  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.

**Table 2.** Desorption energies,  $E_d$  (eV) for {100}, {111} and {110} surfaces.  $H_t$  and  $O_t$  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.

Desorption energy, $E_d$ (eV)			
Defect	{100}	{111}	{110}
$V_{\text{CO}}$	6.08	2.81	4.81
$V_{\text{CH}}$	11.57	10.16	10.86
$H_t-V_{\text{O}}$	2.48	2.56	1.12
$H_t-V_{\text{H}}$	4.50	4.37	3.30
$O_t-V_{\text{O}}$	2.29	1.60	0.15
$O_t-V_{\text{H}}$	4.28	4.65	2.85
$H_t-V_{\text{CO}}$	3.55	5.15	4.06
$O_t-V_{\text{CO}}$	4.33	3.85	2.72
$O_t-V_{\text{CH}}$	10.95	11.85	11.08
$H_t-V_{\text{CH}}$	10.54	11.92	11.02



**Figure 7.** Structures with large crystal planes formed by anisotropic EBIE. (a): A  $\{110\}$  sided inverse pyramid. Such structures occasionally form in random locations during large area anisotropic etches and are attributed to subsurface defects. (b - d): Beginning with an array of approximately circular holes etched under isotropic conditions (b), inverse pyramid - like structures evolve during subsequent anisotropic EBIE of the region. (c) and (d) show the array after 16 and 32 hours of EBIE performed using a low electron flux and  $R_p$  of 2.2. (e) and (f) show closeups of individual structures from (c) and (d) respectively. (g - i): A similar anisotropic etch process was performed on individual circular holes similar to those in (b). (g): A structure formed from a circular hole after 40 mins of anisotropic EBIE of the surrounding region. (h - i): Evolution of a separate circular hole, shown here after 30 (h) and 60 (i) minutes of anisotropic EBIE. The typical evolution observed involves formation of both  $\{111\}$  and  $\{110\}$  planes with the  $\{111\}$  planes receding and roughening whilst 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  $\mu\text{m}$ . The  $\{100\}$  crystal directions indicated in (b) apply to all images. The images in (j - l) were taken at 45, 35 and 30  $^\circ$  tilt respectively.

The desorption energy for CO is far lower than for CH on all considered pristine diamond planes (top row of table 2), indicating a fundamental role of oxygen adatoms in weakening C-C surface bonds. Conversely, a high  $E_d$  for CH suggest 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  $\text{O}_2$  and pure  $\text{H}_2$  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  $\text{H}_2$  and  $\text{O}_2$ . However, we must emphasise 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.<sup>56,57</sup> 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 structures with smooth  $\{110\}$  plane sidewalls can form within etch pits. An example is shown in figure 7(a) and the etch pit shown in figure 2(d) shows a less evolved example. We attribute

their nucleation to the presence of subsurface defects, and employ a two step etch process to fabricate similar structures deterministically. An array of approximately circular holes is first made using isotropic conditions (pure  $O_2$ , fig. 7(b)). This is then followed by etching of the entire array under highly anisotropic conditions ( $H_2 + O_2$ ,  $R_p \approx 2.2$ ). Plasma is used during both steps to ensure a high degree of isotropy and anisotropy, respectively. Figure 7(c) & (d) illustrates the time-evolution of the array by images acquired at different stages during anisotropic etching. Figure 7(e) & (f) show close-ups of individual structures from (c) and (d) respectively. The holes initially evolve into structures with smooth  $\{111\}$  planes at the top, 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 7(g - i) show 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 fig. 5). The inclination of the smooth sidewalls was measured from these images to be  $-45 \pm 3^\circ$  with respect to the  $\{100\}$  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 7(j-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 (fig. 7(l)) 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 fig. 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 adsor-

bates 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  $H_2O$  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 ultra-pure deionised water was first performed for 30 minutes each. Immersion in boiling piranha solution (3:1 mixture of 96 %  $H_2SO_4$ :30 %  $H_2O_2$ ) at  $155^\circ C$  with periodic replenishment of  $H_2O_2$  was then performed for 30 minutes. This was followed by rinsing with DI water, a second piranha solution immersion with ultrasonication at room temperature, ultrasonication with ultra-pure 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 (EVAC-TRON 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 ultra-pure deionised water. Gas input lines pass through a cold trap, held at 116 K for precursors other than  $H_2O$ . 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  $2.9 \times 2.0 \mu m$  region of the sample surface to an average electron flux of  $1.5 \times 10^{10} e^- \mu m^{-2} s^{-1}$ . The raster consisted of 484 lines per frame, 30 nm pitch between lines and 1.68 ms linetime. An analog sine wave voltage signal was connected to the horizontal scan coil ('x-direction'), and was therefore not discretized to individual dwell points. Each irradiation was performed for 20 minutes excepting the pits shown in fig. 4(c, d, e, g & h) which were etched for 40 minutes. A pressure of approximately



9 Pa was used for all EBIE experiments utilizing a single precursor. For the experiments involving H<sub>2</sub> & O<sub>2</sub> mixing, the total chamber pressure was 9 ± 1.5 Pa. The pit shown in figure 2(g) 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 fig. 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.

**Figure 7:** The inverse pyramid shown in (a) formed during EBIE of a 6.0 x 4.14 μm region with the same beam parameters described above and a H<sub>2</sub>:O<sub>2</sub> ratio of 0.78. (b): 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<sup>6</sup> pixels with 10 μs pixel dwell time. The etch frames and beam currents used were 18.5x18.5 μm, 21 nA for the array (fig. 7(c-f)) and 3.5x3.5 μm, 5.6 nA for individual etches (fig. 7(g-i)), resulting in electron fluxes of 3.81 x 10<sup>8</sup> and 2.85 x 10<sup>9</sup> e<sup>-</sup> μm<sup>-2</sup> s<sup>-1</sup> respectively. A H<sub>2</sub>:O<sub>2</sub> ratio of 0 and 2.2 with 10 Pa total chamber pressure were 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 hydrogen silsesquioxane (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 x 2.7 μm region with the disk centered in the frame. Etch times were 4 hours and 1 hour for the pillars shown in (j - k) and (l) respectively.

### DFT computational method

The calculations presented in this work were performed using a Density Functional Theory approach, within the Generalized Gradient Approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional for the Exchange-Correlation term.<sup>58</sup> 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.<sup>59,60</sup> Double-zeta plus polarization orbitals (DZP) were applied, and the cut-off energy for the valence electrons was set to 750 Ry.<sup>60,61</sup> Γ point calculations have been used for a (6×6), (6×4) and (4×4) expansion of the {111}, {110} and reconstructed {100} surfaces, consisting of 12 atomic layers, with a vacuum gap of ca. 25 Å. Full geometry optimization has been carried out for each system, and the convergence criteria for the energy and forces are 10<sup>-4</sup> eV and 10<sup>-2</sup> eV/Å, respectively.

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**Supporting Information Available:** 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 in the SI. There are also further DFT calculations including bond lengths, surface formation energies,  $E_a$  and  $E_d$  for species other than O and H and schematics illustrating adsorption geometries. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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# Graphical TOC Entry

