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ARTICLE TYPE

# Electrochemical “Read-Write” Microscale Patterning of Boron Doped Diamond Electrodes

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Scanning electrochemical cell microscopy is utilised as a read-write pipette-based probe to both electrochemically modify the local surface chemistry of boron doped diamond and “read” the resulting modification, at the micron scale. In this specific application, localised electrochemical oxidation results in conversion of the H-terminated surface to –O, electrochemically visualised by monitoring the current change for reduction of  $\text{Ru}(\text{NH}_3)_6^{3+}$ . This methodology, in general, provides a platform for read-write analysis of electrodes, opening up new analysis avenues, particularly as the pipette can be viewed as a microfluidic device.

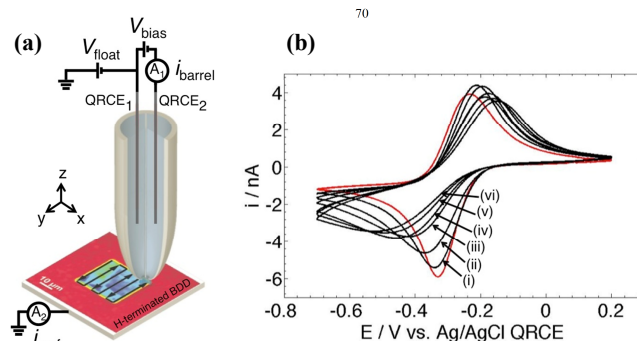
Controlling the surface chemistry of electrodes is of great importance for the fabrication of sensors in order to improve electrocatalytic performance and enable an assessment of the impact of surface chemistry on the fundamentals of electrochemical phenomena.<sup>1</sup> Patterning of an electrode can lead to higher detection sensitivities, the ability to both sense multiple analytes and make many measurements on one device. Various approaches to patterning have been proposed, the most popular being lithography, where a mask is used to define regions of the surface for subsequent chemical modification. For conventional metal electrodes, self-assembled monolayers, or physisorbed molecules are typically attached to the localised region of interest in order to tailor the molecular surface chemistry.<sup>2</sup> However, this is a write-only process and other techniques must then be utilised to “read” the resulting chemical functionalization.

In the electrochemistry field, conducting boron doped diamond (BDD) electrodes are proving popular due to their biocompatibility, larger solvent windows (compared to a metal electrode), low background currents and processability. Chemical functionalisation of BDD is particularly attractive due to the considerable stability of the surface chemical bonds.<sup>3</sup> At the simplest level, diamond can be either –H or –O terminated. For example, diamond materials grown under a hydrogen atmosphere are H-terminated, rendering the surface hydrophobic. Alternatively, oxygen (-O) termination is possible using a variety of methods including, for example, boiling in acid, exposure to an  $\text{O}_2$  plasma or anodic polarisation.<sup>4</sup> O-terminated surfaces are hydrophilic. Other methods also exist for terminating the surface with a wide variety of more complex molecular species.<sup>3</sup> On insulating diamond, H-termination results in a measurable surface

conductivity, due to surface transfer doping and an increase in available charge carriers.<sup>5</sup> Hence, for diamond, changing surface termination not only influences the surface chemistry but can also affect the electrical characteristics. We exploit this phenomenon for the read-write technology described herein.

The amount of boron doping in diamond controls the electrical properties. For metal-like behaviour, the diamond must be doped with  $> 10^{20}$  B atoms  $\text{cm}^{-3}$ .<sup>6</sup> Boron levels less than this result in p-type semi-conducting behaviour. Microscale chemical patterning of diamond surfaces has been achieved using several techniques including lithographic chemical/molecular functionalization,<sup>7</sup> and scanning probe modification.<sup>8,9,10</sup> In the latter, an anodically biased tip was used to (electro)chemically pattern regions of either a bare (H-terminated) surface<sup>8,9</sup> or one which had been chemically modified,<sup>10</sup> in air. The tip was also used to image the resulting modification by either recording the change in surface topography<sup>10</sup> or local conductivity.<sup>9</sup>

In this communication we present a new electrochemical approach to the microscale “read-write” chemical patterning of diamond electrodes using scanning electrochemical cell microscopy (SECCM), as illustrated in Figure 1a.<sup>11,12</sup>



**Figure 1:** (a) Illustration of the SECCM set-up, showing the use of a theta capillary of  $\sim \mu\text{m}$  diameter to both locally modify the surface (write) and then subsequently read the resulting surface change. (b) Successive CVs recorded at  $0.1 \text{ V s}^{-1}$  after  $\times 5$ , 1 s anodic pulses at  $+1.5 \text{ V}$ , recorded successively for a total of 30 pulses, for the reduction of  $1 \text{ mM Ru}(\text{NH}_3)_6^{3+}$  in  $0.1 \text{ M KNO}_3$  on H-terminated semiconducting BDD, using a microcapillary of diameter  $\sim 52 \mu\text{m}$ .

SECCM employs a scanning dual channel (theta) pipette, filled with the electrolyte solution of interest and a quasi-reference counter electrode (QRCE) in each channel. This constitutes a conductimetric cell. A further dynamic electrochemical cell is created when the meniscus protruding from the end of the pipette makes contact with the (working) electrode substrate, biased at a potential, with respect to the QRCEs, to drive an electrochemical process of interest.

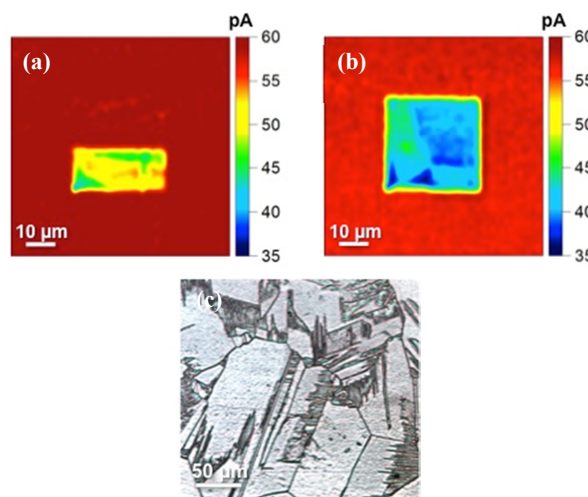
In this application the SECCM tip is used to both spatially convert the electrode surface from -H to O-termination using anodic polarisation (write) and image the resulting change in surface termination using an electrochemical approach (read), at the micron scale. Here we employ semi-conducting BDD in conjunction with the outer sphere redox mediator  $\text{Ru}(\text{NH}_3)_6^{3+}$ ; the reduction potential of which lies in the band gap of semi-conducting p-type BDD.<sup>13</sup> Alternatively, conducting BDD could be utilised in partnership with inner sphere redox probes. Experiments initially explored the effect of applied anodic potential on the electrochemical response of freestanding H-terminated semi-conducting polycrystalline BDD ( $2 \times 10^{18}$  boron atoms  $\text{cm}^{-3}$ ; grain size  $\sim 7 - 100 \mu\text{m}$ ,<sup>13</sup> grown by Element Six, Harwell, UK) using a larger scale microcapillary technique.<sup>14</sup> The BDD surface was polished to an  $\sim \text{nm}$  finish using a diamond lapping technique.<sup>13</sup> Briefly, the set-up employed a glass borosilicate capillary pulled and polished to an inner diameter of  $\sim 52 \mu\text{m}$ , filled with the solution of interest (defined below) and containing an Ag/AgCl (AgCl-coated Ag wire) QRCE. The meniscus from the tip was positioned on a localised region of the surface using  $x$ - $y$ - $z$  micropositioners, aided by visualisation from a high magnification camera (Pixelink PL-B776U).

Figure 1b shows cyclic voltammograms (CVs) recorded at a scan rate of  $0.1 \text{ V s}^{-1}$  for reduction of  $\text{Ru}(\text{NH}_3)_6^{3+}$  (1 mM) in 0.1 M  $\text{KNO}_3$  on a H-terminated semiconducting BDD electrode,<sup>13, 15</sup> functionalised before use with a hydrogen plasma,<sup>13</sup> and confirmed to be hydrophobic by contact angle analysis.<sup>16</sup> A typical initial CV, shown in Figure 1 (red), with a start and end potential of 0.2 V, and a reverse potential of -0.7 V, was recorded on the freshly H-terminated surface. With the capillary held in the same position, the electrode was then subject to anodic polarisation at +1.5 V vs. Ag/AgCl QRCE for 1 s, followed by a wait period of 5 s at the start potential and a CV was recorded again. This procedure was repeated 30 times. The resulting CVs are shown in Figure 1 after (i) 5; (ii) 10; (iii) 15; (iv) 20; (v) 25 and (vi) 30, 1 s pulses.

On O-terminated semi-conducting BDD, electron transfer (ET) has been shown to be sluggish for  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ .<sup>13</sup> However, as shown here, surface transfer doping, due to H-termination<sup>17</sup> results in a peak to peak separation,  $\Delta E_p$ , for the redox couple  $\text{Ru}(\text{NH}_3)_6^{3+/2+}$  of  $\sim 96 \text{ mV}$ , indicative of significantly faster ET kinetics than would be expected for the O-terminated surface. Notably, after just 1 s of anodic treatment, on the freshly H-terminated surface,  $\Delta E_p$  is observed to increase to 116 mV. It is well documented that anodic polarisation of the BDD surface leads to a change in surface termination,<sup>4c,13</sup> the relative contributions of different -O groups formed on the surface dependent on the polycrystallinity of the material and the extent of the treatment. As shown in Figure 1, repeated anodic polarisation leads to a significant increase in  $\Delta E_p$  due to the

removal of local charge carriers as the surface termination changes from -H to -O. After 30 s of anodic treatment  $\Delta E_p$  is  $\sim 378 \text{ mV}$ .<sup>16</sup> Note that such effects would be unlikely if the material was doped to be metal-like as the number of available charge carriers would be sufficiently high to ensure fast ET irrespective of surface termination.<sup>13</sup> For example, H- and O-terminated metallic doped BDD macrodisc electrodes show very similar CV responses towards the reduction of  $\text{Ru}(\text{NH}_3)_6^{3+}$ .<sup>13</sup>

The premise that the local BDD surface termination could be both modified (write) and detected electrochemically (read) was further investigated using SECCM (Figure 1a). In brief, a borosilicate theta capillary of inner diameter of *ca.*  $1-2 \mu\text{m}$ , filled with solution (2 mM  $\text{Ru}(\text{NH}_3)_6^{3+}$  in 50 mM  $\text{KNO}_3$ ) was used as the read-write probe. A potential,  $V_{\text{bias}}$  of 200 mV was applied between the QRCEs in each barrel. During approach to the surface, a small oscillation (60 nm) in the  $z$ -position of the probe was applied. When the meniscus came into contact with the surface, an alternating current component,  $i_{\text{AC}}$ , in the current between the barrels was established; which was very sensitive to the tip-substrate separation. In SECCM,  $i_{\text{AC}}$  is used as a set point for electrochemical imaging, in this case to maintain contact between the meniscus and diamond surface. For the studies herein, the  $i_{\text{AC}}$  values were in the range 80-120 pA, about 1 % of the mean conductance current,  $i_{\text{barrel}}$ , and about two orders of magnitude above the background (residual) value of  $i_{\text{AC}}$  when the probe was away from the surface. The BDD electrode was grounded and the effective potential controlled by floating the conductimetric cell at a potential,  $V_{\text{float}}$ , so that the potential of the diamond substrate was  $-(V_{\text{float}} + V_{\text{bias}}/2)$  with respect to the QRCE potential.<sup>18</sup>



**Figure 2:** (a) and (b) SECCM read-write scans of selected regions on H-terminated BDD, anodically oxidised by biasing at +1.5 V (write) and imaged (read) at -0.3 V using a SECCM probe of  $\sim \mu\text{m}$  diameter, filled with 2 mM  $\text{Ru}(\text{NH}_3)_6^{3+}$  in 50 mM  $\text{KNO}_3$ . (c) Optical image of the grain structure of the polycrystalline BDD electrode employed.

In initial SECCM experiments, the SECCM probe was used to anodically oxidise a small area ( $10 \mu\text{m} \times 20 \mu\text{m}$ ) of the H-terminated semiconducting electrode. For the first half of a  $20 \mu\text{m} \times 20 \mu\text{m}$  scan (scanning bottom to top) an effective anodic

oxidation potential of +1.5 V was applied and then switched to -0.3 V for the remainder of the scan, which is only sufficient to reduce  $\text{Ru}(\text{NH}_3)_6^{3+}$  on the H-terminated surface (Figure 1b). To view the resulting surface modification, SECCM imaging was carried out over a larger  $50 \mu\text{m} \times 50 \mu\text{m}$  scan area, with the area previously scanned in the centre. An effective potential of -0.3 V was applied to the electrode, and the electrochemical current recorded every  $1 \mu\text{m}$  (tip scan speed  $1 \mu\text{m s}^{-1}$ ) and plotted as an activity map, as shown in Figure 2a.

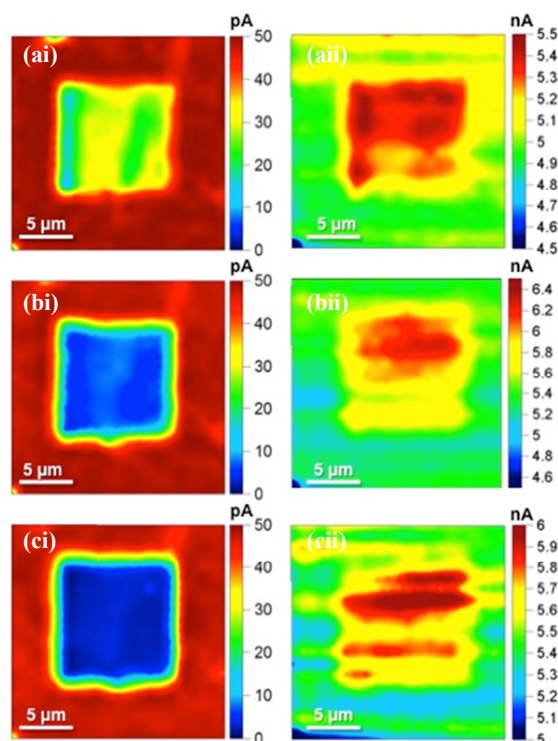
As seen in Figure 2a, anodic treatment results in a measurably smaller current for reduction of  $\text{Ru}(\text{NH}_3)_6^{3+}$  due to partial anodic removal of the H-termination layer, qualitatively consistent with the data in Figure 1. The residence time of the meniscus in the vicinity of the electrode surface was  $\sim 1$  s during local modification (writing) and subsequent activity imaging (reading), and this is clearly sufficient to modify the surface termination. The current response in the top half of the scan stays relatively constant ( $58.9 \pm 0.6$  pA,  $n = 173$  pixels) and is similar to that seen in the larger  $50 \mu\text{m} \times 50 \mu\text{m}$  scan area ( $58.1 \pm 2.9$  pA,  $n = 173$  pixels). The similarities of the currents recorded in the H-terminated regions of the surface suggest that no significant change in termination was caused by either the physical act of scanning across the surface, or during application of the -0.3 V potential, during the 'write process'.

Interestingly, the area of the activity scan modified by anodic polarisation displays a heterogeneously varying current, reminiscent of earlier work on metallic O-terminated polycrystalline BDD which showed that differently doped grains (facet) have different electroactivity.<sup>19,20</sup> In order to investigate this further, a full  $20 \mu\text{m} \times 20 \mu\text{m}$  oxidising scan was performed in a new area of the sample, and then imaged at -0.3 V over  $50 \mu\text{m} \times 50 \mu\text{m}$ , to promote the reduction of  $\text{Ru}(\text{NH}_3)_6^{3+}$ , using the same conditions as before (Figure 2b). The decreased activity current (read) magnitude in the region of the anodic (write) pretreatment is again apparent, as are angular features demarking areas of different activity. These different zones most likely represent the different crystal facets associated with this polycrystalline material, as shown optically in Figure 2c, which contain differing amounts of boron, and which may also be subject to different degrees of oxygen termination (or depletion of charge carriers), during the 'write' process. In summary, Figure 2b demonstrates that using SECCM it is possible to confine the electrochemical patterning process to  $\sim$  micron sized areas on the surface. It should also be possible to achieve even higher spatial resolution in the future by employing smaller imaging pipettes.<sup>21</sup>

It is of interest to investigate the extent to which the electrochemical activity of the diamond surface can be tuned. A smaller scan area of  $10 \mu\text{m} \times 10 \mu\text{m}$  was electrochemically oxidised by scanning the SECCM meniscus over the surface (bottom to top) a total of three times, with the surface biased at +1.5 V ( $1 \mu\text{m s}^{-1}$  scan speed). Imaging took place after each oxidative scan at an effective potential of -0.3 V, over a scan area of  $20 \mu\text{m} \times 20 \mu\text{m}$  to capture (read) the activity of the modified area and the immediate surrounding (unmodified) area. Figure 3 shows (i) the BDD electrochemical current response and (ii) the conductance current response between the two channels of the

theta pipette for the reduction of  $2 \text{ mM Ru}(\text{NH}_3)_6^{3+}$  after the (a) first; (b) second and (c) third oxidative (modification) scans.

Figures 3ai to ci, show that there is a gradual decrease in  $\text{Ru}(\text{NH}_3)_6^{3+}$  reductive currents in the square region with consecutive scans, indicating the gradual removal of the H-termination layer with subsequent oxidative scans. After three scans the currents in the central region of the O-terminated area of the surface have dropped by over 90%, compared to the surrounding H-terminated regions. Figures 3aii – cii are further illuminating on the effect of surface termination. These show the dc conductance current between the QRCEs in the barrels of the theta pipette, highlighting that in the modified region this increases by about 20% which can be attributed to a change in the meniscus contact<sup>18</sup> due to increased wetting of the surface in the O-terminated regions.



**Figure 3:** SECCM read-write (i) electrochemical current maps and (ii) tip dc conductance maps recorded simultaneously, after three consecutive oxidative scans (a) to (c), recorded with (i) the BDD electrode biased at -0.3 V (read), after writing took place at +1.5 V and (ii) +200 mV applied between the two QRCEs in each barrel, in a theta capillary of  $\sim \mu\text{m}$  diameter, filled with  $2 \text{ mM Ru}(\text{NH}_3)_6^{3+}$  and  $50 \text{ mM KNO}_3$  on H-terminated BDD.

In summary, the studies herein show that SECCM can be used to alter the surface properties of a diamond electrode such that electrochemistry is inhibited in some regions, while being relatively facile in others. This opens up the prospect of surface patterning and the creation on electrochemical (and electronic) devices by the local chemical modification of diamond. On a conducting BDD surface we envisage alternative inner sphere redox probes could be employed to read the modification process. Furthermore, it has been successfully demonstrated that the



surface termination of diamond electrode can be both modified (write) and detected (read) using SECCM imaging, with a simple pipette. This also provides a platform for write-read analysis of other surfaces, opening up new avenues for analysis, particularly as the pipette can be viewed as a microfluidic device.<sup>22</sup> With further work, it may also be possible to effect write-read-erase strategies on conducting diamond in view of the possibility of creating H-terminated surfaces electrochemically.<sup>23</sup>

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## Notes and references

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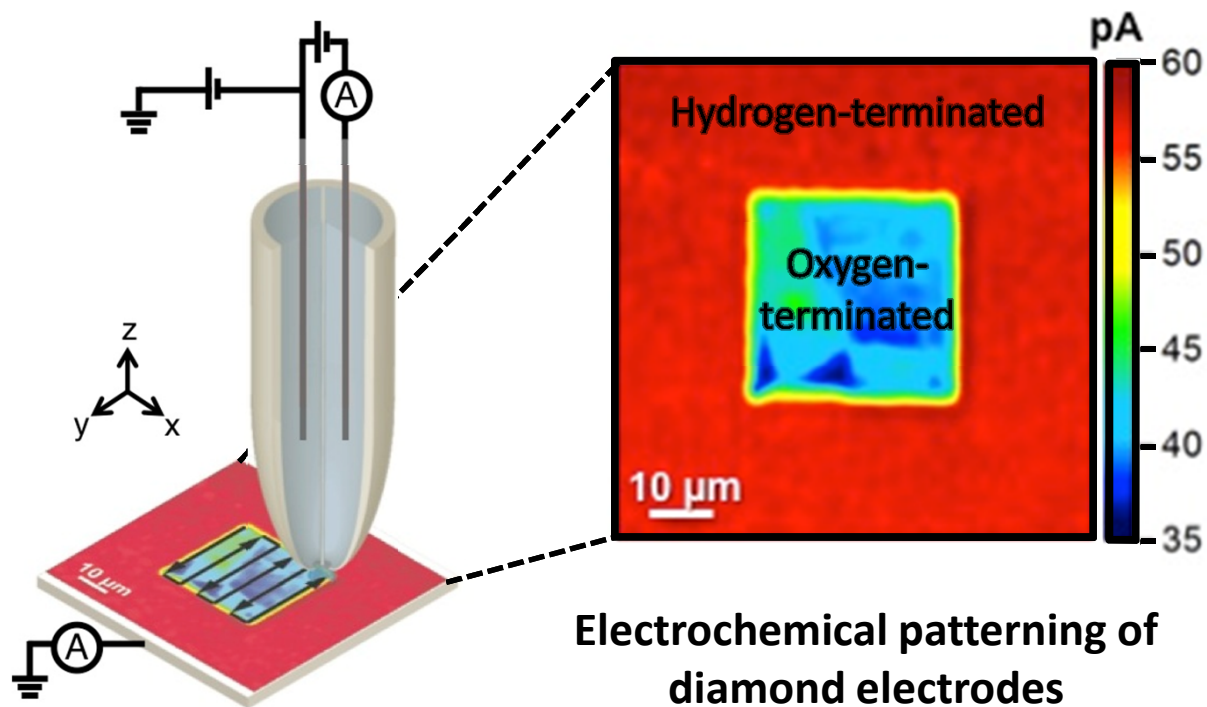
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We report the use of scanning electrochemical cell microscopy (SECCM) for the electrochemical “read-write” patterning of boron doped diamond electrodes