Stability of oxygenated groups on pristine and defective diamond surfaces

Eliezer Oliveira1,2 · Chenxi Li3 · Xiang Zhang3 · Anand Puthirath3 · Mahesh R. Neupane4 · James Weil4 · A. Glen Birdwell4 · Tony Ivanov4 · Seoyun Kong3 · Tia Grey3 · Harikishan Kannan3 · Robert Vajtai3 · Douglas Galvao1,2 · Pulickel Ajayan3

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Abstract
The surface functionalization of diamonds has been extensively studied through a variety of techniques, such as controlled oxidation. Several oxygen groups have been detected on oxidized diamonds, such as C–O–C (ester), C=O (ketonic), and C–OH (hydroxyl). However, the composition and relative concentration of these groups on diamond surfaces can be affected by the type of oxygenation treatment and the diamond surface quality. To investigate the stability of the oxygenated groups at specific diamond surfaces, we evaluated through fully atomistic reactive (ReaxFF force field) molecular mechanics (FARMM) simulations, the formation energies of the C=O, C–O–C, and C–OH groups on pristine and defective diamond surfaces (110), (111), and (311). According to our findings, the C–OH group has the lowest formation energy on a perfect (110) surface, while the C–O–C is favored on a defective surface. As for the (111) surface, the C–O–C group is the most stable for both pristine and defective surfaces. Similarly, C–O–C group is also the most stable one on the defective/perfect (311) surface. In this way, our results suggest that if, in a diamond film, the (110) surface is the major exposed facet, the most adsorbed oxygen group could be either C–OH or C–O–C, in which the C–O–C would depend on the level of surface defects.

Introduction
Recently, the oxidation of polycrystalline diamond film (PCD) was investigated using wet and dry methods, such as H2SO4/HNO3 acid with various ratios at different temperatures, aqua regia, Fenton solution, Hummer’s method, piranha solution, O2 plasma, and UV ozone [1, 2]. The best oxidation performance was reached when it was used H2SO4/HNO3 in a ratio 5:1 at 360 °C, achieving an oxygen content close to 10%.

The high-resolution spectrum of XPS shows that different carbon–oxygen groups can be found on PCD diamond surfaces depending on the oxygenation treatments used, such as C–O–C, C=O, and C–OH. Some dry oxygenation methods, such as O2 plasma-treated, produce a high concentration of C–O–C, while the UV ozone one results in C–OH in greater number [1]. As for the wet oxidation method, the C–OH group is produced in a higher concentration in comparison with the other carbon–oxygen groups.

As can be seen, depending on the different used oxidation treatment, different carbon–oxygen groups can be found in preponderance on the PCD diamond surfaces. Also, depending on the diamond facets exposed on PCD, as well as on defects on the surfaces, this can influence the preference of a specific carbon–oxygen group formation. Then, in this work, we performed a theoretical study using fully atomistic reactive molecular mechanics (FARMM) to investigate the possible reasons that can affect the carbon–oxygen group formation on PCD surfaces. Our results suggest that, due to the presence of different diamond surfaces exposed to the oxidation process on PCD, as well the presence of surface defects, these are the dominant features to alter the proportion of different oxygenated groups formed at diamond surfaces.
Materials and methods

To explore the energy stability of C=O, C–O–C, and C–OH oxygenated groups that could be found on the diamond surfaces after the oxygenation process, we have performed fully atomistic reactive molecular mechanics (FARMM) simulations using ReaxFF [3] potential. In general, this kind of study can be performed using Density Functional Theory (DFT) methods, but we decided to use the FARMM because it allows us to simulate larger systems at a lower computational cost, allowing more realistically structural models of the surface oxygenation percentages (at most 10% in the experiments). Regarding the diamond surfaces that will be used in our study, we selected the surfaces (110), (111), and (311) because they were the most observed in the PCD used in the experiments [1]. We like to stress that these diamond surfaces are different from the ones that were already studied in the literature [4–8]. Figure 1a presents the structural models for these pristine diamond surfaces. For each diamond surface, we created slabs of ~ 380 carbon atoms and of sizes of ~ 14 × 14 × 10 Å. The positions of the carbon atoms in the bottom two layers were kept constrained in the diamond bulk positions to mimic bulk-like slabs.

The geometrical optimizations were performed with a conjugate gradient (CG) technique, adopting the energy and force convergence tolerances of 0.001 and 0.5 kcal/mol/Å, respectively.

To investigate the energy stability of each oxygenated group tested in this work, after the geometry optimizations, we estimated their binding energy using the following equation:

\[ \text{BE}_{\text{OG}} = E_{\text{(D+OG)}} - E_{\text{(D)}} - E_{\text{OG}} \]

in which the \( \text{BE}_{\text{OG}} \) is the binding energy of the oxygenated group, \( E_{\text{(D+OG)}} \) is the total energy of the diamond slab with the chemisorbed oxygenated group, \( E_{\text{(D)}} \) is the energy of the bare diamond slab, and \( E_{\text{OG}} \) is the total energy of the oxygenated group. Using the binding energy as defined in Eq. 1, the more negative is \( \text{BE}_{\text{OG}} \), the more stable will be the specific oxygenated group on the diamond surface. All these simulations were done with the LAMMPS software [9] and the periodic boundary conditions (PBC) were used along the x and y-directions to mimic infinite slabs.

Results and discussions

As can be seen from Fig. 1, a perfect (110) surface does not exhibit any surface reconstruction and the most exposed atoms form a zig-zag configuration, which results in one dangling bond for each exposed carbon atom. To test the stability of the C=O group, we can see that it is necessary to have two dangling bonds for the carbon atom. Then, we created a (110) surface with ~ 20% of randomly distributed carbon vacancies at the carbon zig-zag configuration in order to have carbon atoms at the surface with two dangling bonds. This defective diamond surface is shown in Fig. 1b, in which the atoms highlighted in red represent the most exposed ones. We tested the C–O–C, C=O, and C–OH on the defective (110) surface in the configurations shown in Fig. 2a–e. In the case of the C–O–C and C–OH groups, two different configurations were tested (see Fig. 2a, b, d and e). After the geometry optimizations, we found the following bond lengths: 1.45 Å for C–O bonds in C–O–C–1 (Fig. 2(1)); 1.60 Å for C–O bonds in C–O–C–2 (Fig. 2b); 1.29 Å for C=O bond (Fig. 2c); 1.41 and 0.98 Å for, respectively, C–O and O–H bonds in C–OH–1 (Fig. 2d); and 1.46 and 0.95 Å for, respectively, C–O and O–H bonds in C–OH–2 (Fig. 2e).

Table 1 presents the binding energies for these oxygenated groups on the (110) surface. As can be seen, the C–O–C–1 (Fig. 2a) is the most stable one, followed by the C=O, C–OH–1 (Fig. 2d), C–O–C–2 (Fig. 2b), and C–OH–2 (Fig. 2e). We see that the presence of defects on the (110) surface changes the stability of the oxygenated groups. Considering a perfect (110) surface, in which it is possible to have only C–O–C and C–OH groups, the C–OH will be the most stable one.

Considering the surface (111), its most stable configuration presents a surface reconstruction 2 × 1 [10–14], which results in carbon atoms with one dangling bond each at the surface. As discussed before, to form a C=O bond, it is necessary a carbon atom with 2 dangling bonds. To circumvent this issue, we created a (111) surface with ~ 20% of randomly distributed carbon vacancies, which results in surface carbon atoms with up to 2 dangling bonds (see Fig. 1b, in which the most exposed carbon atoms on the surface are highlighted in yellow). Figure 2f–j presents the tested configurations for the C–O–C, C=O, and C–OH groups.
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In these cases were as follows: 1.50 Å for C-O bonds in C–O–C-1 in Fig. 2f; 1.44 Å for C-O bonds in C–O–C-2 in Fig. 2g; 1.41 Å for C=O bond shown in Fig. 2h; 1.41 and 0.98 Å for C-O and O–H bonds, respectively, in C–OH-1 in Fig. 2i; and 1.48 and 0.93 Å for C-O and O–H bonds, respectively, in C–OH-2 in Fig. 2j. From the estimated binding energies presented in Table 1, we can see that the C–OH-1 (Fig. 2i) is the most stable on the surface (111), followed by the C–O–C-2 (Fig. 2g). The C–O–C-1, C=O, and C–OH-2 are not stable on this surface.

On the surface (311), we see that we have carbon atoms with one and two dangling bonds (see Fig. 1a in which the carbon atoms with one dangling bond are highlighted in yellow, and with two dangling bonds are highlighted in orange). In Fig. 2k–o, we present the C–O–C, C=O, and C–OH on the (311) surface in the configurations shown in Fig. 2k–o. From the energy minimized structures, we can find the following bond lengths: 1.44 Å for C-O bonds in C–O–C-1 in Fig. 2k; 1.60 Å for C–O bonds in C–O–C-2 in Fig. 2l; 1.28 Å for C=O bond in Fig. 2m; 1.40 and 0.98 Å for, respectively, C–O and O–H bonds in C–OH-1 in Fig. 2n; and 1.45 and 0.96 Å for, respectively, C–O and O–H bonds in C–OH-2 in Fig. 2o. According to the binding energies presented in Table 1, the most stable group is the C–O–C-1 (Fig. 2k), followed by the C=O (Fig. 2m) and C–OH-2 (Fig. 2o). The C–O–C-2 (Fig. 2l) and C–OH-1 (Fig. 2n) are not stable on surface (311).

Conclusions

According to our study, the C–OH group is the most stable one when we are considering (110) and (111) perfect (non-defective) diamond surfaces. However, the C–OH groups may not be the most stable ones when it is taken into account the presence of defects on the surfaces. In the case of the (311) surface, we see that the C–O–C group is the most stable, but in general, this surface is less exposed to oxidation than the (110) one, which suggests that this surface may not contribute significantly to the number of incorporated oxygenated groups in diamonds. In general, our results suggest that if the oxidation process causes significant structural damages on the diamond surfaces or if the diamond surfaces have poor quality, oxygenated groups other than C–OH may be found in greater amounts.

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Table 1 Theoretical binding energies of the C–O–C, C=O, and C–OH groups on (110), (111), and (311) diamond surfaces

| Surface | Binding energy (eV) |
|---------|---------------------|
| (110)   | C–O–C-1  | C–O–C-2  | C=O    | C–OH-1  | C–OH-2  |
|         | – 8.49   | – 3.93   | – 6.58 | – 4.05  | – 3.33  |
| (111)   | C–O–C-1  | C–O–C-2  | C=O    | C–OH-1  | C–OH-2  |
|         | 3.32     | 4.93     | 14.06  | 5.40    | 7.23    |
| (311)   | C–O–C-1  | C–O–C-2  | C=O    | C–OH-1  | C–OH-2  |
|         | – 9.22   | 2.78     | – 6.63 | 1.49    | – 1.07  |

See in Fig. 2 the corresponding configurations of each carbon–oxygen group at the diamond surface.

Fig. 2 Configurations for the carbon–oxygen groups on diamond surfaces used for binding energy estimates: a C–O–C in conformation 1 (C–O–C-1), b C–O–C in conformation 2 (C–O–C-2), c C=O, d C–OH in conformation 1 (C–OH-1), and e C–OH in conformation 2 (C–OH-2) on a (110) surface, f C–O–C in conformation 1 (C–O–C-1), g C–O–C in conformation 2 (C–O–C-2), h C=O, i C–OH in conformation 1 (C–OH-1), and j C–OH in conformation 2 (C–OH-2) on a (111) surface, k C–O–C in conformation 1 (C–O–C-1), l C–O–C in conformation 2 (C–O–C-2), m C=O, n C–OH in conformation 1 (C–OH-1), and o C–OH in conformation 2 (C–OH-2) on a (311) diamond surface. The cyan, red, and white atoms are, respectively, carbon, oxygen, and hydrogen.
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