
J. M. A. Beattie, J. P. Goss, M. J. Rayson and P. R. Briddon

School of Engineering, University of Newcastle, Newcastle upon Tyne NE1 1TRU

Control over the chemical termination of diamond surfaces has shown great promise in the realization of field-emission applications, the selection of charge states of near-surface color-centers such as NV, and the realisation of surface-conductive channels for electronic device applications. Efficient electron-emission exploiting the negative electron-affinity requires a stable surface treatment that can operate over a useful range of temperatures, for which H-termination fails. For compounds involving oxygen, surface geometry and layer stoichiometry are thought to be critical parameters in engineering the desired affinity. In this study, we show that large negative electron-affinities (−2 to −3 eV) are found for surfaces with an AlO$_3$ stoichiometry, and the formation is exothermic. Higher proportions of Al increases the likelihood of metallic bonding between Al atoms, decreasing the bond-polarity and increasing the electron affinity (making it less negative). AlO$_2$ and Al$_2$O$_3$ unfavorable electron affinities, and have a lower thermal stability.

I. Introduction

The desire to create high-power electronics capable of performing in extreme environments necessitates a robust semiconductor material which can, for example, operate at high-temperature and within environments where radiation is likely to be an issue. Diamond is one such material due to its high breakdown-field, mechanical hardness, wide band-gap and high thermal conductivity$^1$

Surface effects are often significant considerations in the manufacture of devices; surface passivation for the enhancement of electrical properties is already utilized for electron-emission, electrochemistry and catalysis$^{2-4}$. For electron sources, two significant concerns are emission-efficiency and current-density uniformity, both of which are sensitive to electron affinity (EA), crystal orientation and emitter-geometry$^5$. Negative electron-affinity (NEA) surfaces, i.e. where the conduction band at the surface lies above the vacuum-level, are particularly desirable as they enhance electron emission efficiency$^6$.$^7$. $^9$.$^{10}$. H con-

Hydrogen-terminated diamond surfaces are known to exhibit an NEA$^8$: C$^-$−H$^+$ surface dipoles represent a upward potential step moving into the diamond from the vacuum, sufficient to place the conduction-band minimum above vacuum. The measured and calculated NEA of H-terminated diamond lies in the −1.9 to −1.1 eV range$^{9-12}$. Terminating with a species more electronegative than carbon has the opposite effect, so that, for example, fluorine-termination generates C$^{++}$−F$^-$ dipoles and positive EAs (PEAs) in the 2.1−2.5 eV range$^{13,14}$. Other halogen terminations such as chlorine exhibit PEAs in the region of 0.8 eV$^7$.

Although H-terminated diamond yields an NEA, its value is relatively small and, arguably more significantly, hydrogen begins to desorb$^{15}$ at 400°C in vacuum. H continues to desorb up to 1200°C where the resulting untermi-

Many other terminations have been explored in the pursuit of a large, stable NEA, including metals and metal-oxides$^{17-20}$. Amongst the metal oxides$^{21}$, copper oxide produces a small NEA of −1.2 eV and low thermal stability, whereas titanium oxide has a sizeable adsorption energy of −7.6 eV per Ti atom and a large NEA of −3.1 eV. Cesium oxide$^{22}$ coated surfaces produce an NEA of −1.3 eV, and X-ray photoelectron spectroscopy reveals this condition is thermally stable up to 500°C. Theoretically, lithium oxide terminated diamond has a binding energy of 4.7 eV/Li atom, and NEAs as large as −3.9 eV$^{23}$.

The range of stabilities and NEAs for different treat-
ments should be considered alongside viability of an in-
dustrial process for production of the coating if the prop-
ties are to be exploited in applications such as field emis-

Aluminium oxide, an inexpensive and ALD compatible$^{24}$ material that is already integrated in technology, might be expected to produce the conditions needed for an NEA. However, to engineer a favorable surface for emission it is necessary to understand how the electron affinity changes as a function of stoichiometry and surface arrangement. The size of the surface electric dipole in-part reflects the difference in the electronega-
tivities of the constituent atoms, which are 2.55, 3.44 and 1.61 for C, O and Al respectively on the Pauling scale$^{25}$. This means that electrons tend to be displaced from Al and C towards O, so that for a diamond–O–Al structure, two sets of opposing dipoles are created. Where the Al–O dipoles dominate, a NEA is expected to arise, but this condition requires both the appropriate stoichiometry to produce favorable oxidation states, and favorable geometry with sufficient Al–O displacement normal to the surface. Since it is known that oxygen-terminated surfaces have a large PEA$^{26,27}$, if insufficient Al-coverage is achieved an NEA is unlikely to be formed, and if there is excessive Al, Al–Al interactions may reduce the Al–O dipoles and also negatively impact the EA. Understanding these mechanisms is crucial for consistent NEAs in device fabrication.

In this paper we present the results of of density func-
tional theory based simulations of Al$_x$O$_y$ layers on (001)-

and (111)-oriented diamond surfaces.
II. Methodology

Structures and electronic properties of (001)- and (111)-oriented aluminium-oxide terminated diamond surfaces have been studied for a variety of Al:O ratios and structural arrangements, simulated using density functional theory (DFT) within the supercell approximation, using the AIMPRO software package.\textsuperscript{28,29} Calculations employ the local density approximation\textsuperscript{30} and norm-conserving, separable pseudo-potentials.\textsuperscript{31} Kohn-Sham functions are represented using basis sets up to and including \(s, p, d\) type Gaussian orbital functions of four widths centered at each atom, resulting in 40 functions per atom. A plane wave expansion of density and Kohn-Sham potential\textsuperscript{32} was used to determine the matrix elements of the Hamiltonian, with a cut off of 200 Ha, yielding well-converged total energies.

Surfaces are modeled using slabs with a minimum of 18 carbon layers and 20 \(\text{Å}\) of vacuum. The surface areas for the (001)- and (111)-oriented surfaces are made up from multiples of \([110]a/2 \times [110]a\) and \([110]a/2 \times [112]a/2\) surface areas, respectively. These conditions isolate the surfaces from each other and have enough material to reasonably describe bulk diamond. Slab surfaces are constructed to ensure inversional symmetry so that the slabs as a whole have no net electric dipole.

Monkhorst-Pack\textsuperscript{33} Brillouin-zone sampling grids of \(10 \times 15 \times 1\) \(k\)-points were used for the smallest cross-sectional area supercells, reducing to \(4 \times 8 \times 1\) with repeats in the [1\(\overline{1}\)0] and [0\(\overline{1}\)0] direction for the (001)-(2\(\times\)1) and (111)-(2\(\times\)1) surfaces respectively to achieve a 6 surface site cell to ease creation of stoichiometric surfaces. For the bulk references the sampling is chosen to be comparable to that of the surface cells.

The diamond lattice parameter is calculated at 3.53 \(\text{Å}\), in excellent agreement with previous calculations\textsuperscript{34,35} and experiment.\textsuperscript{36}

Surface structures were optimised until the iterative energy-reduction and atom displacements were both less than \(10^{-5}\) a.u., and the forces below \(10^{-3}\) a.u. To assess stability, the energy liberated from the addition of the oxide to an unterminated diamond surface is evaluated, expressed as an adsorption energy per surface site: \textsuperscript{37}

\[
E_{\text{surf}} = \frac{1}{2nm} \left( E_{\text{tot}} - E_{\text{slab}} - N_O \mu_O - N_{\text{Al}} \mu_{\text{Al}} \right)
\]  

where \(nm\) is the number of surface sites on an \(n \times m\) surface, the factor of two arises from the two surfaces per slab, \(E_{\text{tot}}\) is the total energy, \(E_{\text{slab}}\) is the energy of the corresponding unterminated slab and \(N_i\) are the numbers of each chemical species in the system. \(\mu_O\) and \(\mu_{\text{Al}}\), the atomic chemical potentials, are taken from thermodynamic equilibrium with bulk \(\text{Al}_2\text{O}_3\), i.e.

\[
E^T(\text{Al}_2\text{O}_3) - 2\mu_{\text{Al}} - 3\mu_O = 0
\]

where \(E^T(\text{Al}_2\text{O}_3)\) is the energy per formula unit of corundum. The range of values for \(\mu_O\) is then fixed at one limit by the energy per atom of oxygen gas, and the result from Eq. 2 when \(\mu_{\text{Al}}\) is the energy per atom of bulk Al. All quoted surface adsorption energies are taken at their most energetically favourable limits.

EAs are obtained by comparison of bulk and slab electrostatic potentials.\textsuperscript{38}

III. Results

We begin with a presentation of the structures obtained for unterminated diamond surfaces.

A. Untermitted surfaces

(001)-(1\(\times\)1) cleaved surfaces have two dangling bonds per surface atom and, in the absence of chemical termination, reconstruct to form the (2\(\times\)1) dimerized surface. The relatively short C–C dimers at 1.37 \(\text{Å}\) (Fig. 1(a)) are characteristic of \(\pi_p\)-bonding, our values in excellent agreement with literature.\textsuperscript{39,40} The metastable (111)-(1\(\times\)1) unterminated surface, Fig. 1(b), undergoes a modest relaxation in the top layer, leaving one dangling bond per surface site. Reconstruction to the (2\(\times\)1) Pandey-chain arrangement (Fig. 1(c)) lowers the energy by 47 meV per surface site, in good agreement with literature values.\textsuperscript{41}

Upon chemical termination the reconstruction is not retained, with, for example, H-termination favoring the 1 \(\times\) 1 structure.\textsuperscript{42}

<table>
<thead>
<tr>
<th>Surface</th>
<th>C</th>
<th>H</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>0.74\noindent, 0.64\textsuperscript{a}</td>
<td>(-2.02\noindent, -1.97\textsuperscript{b})</td>
<td>2.22\textsuperscript{c}, 2.13\textsuperscript{d}\noindent, 2.21\textsuperscript{d}</td>
</tr>
<tr>
<td>(111)</td>
<td>0.29\noindent, 0.38\textsuperscript{a}</td>
<td>(-1.83\noindent, -1.90\textsuperscript{b})</td>
<td>2.57\textsuperscript{c}, 2.60\textsuperscript{d}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} This study
\textsuperscript{b} Ref 13
\textsuperscript{c} Ref 14
\textsuperscript{d} Ref 45

To further validate our approach, we have calculated EAs of the unterminated as well as H and F terminated surfaces. The data listed in Table I show that our estimates are within around 100 meV of literature values.

B. Aluminium oxide

We considered a wide range of structures, varying with either Al or O in contact with diamond. We found diamond–Al–O or mixed C–Al and C–O interfacial bonds significantly less energetically favorable than diamond–O–Al arrangements, and conclude that in equilibrium
III. RESULTS

C–O bonds form the interface between diamond and the oxide. It was previously shown that the interface between diamond and metal-oxides involves oxygen singly bonded to the diamond\textsuperscript{21}, and can be thought of as diamond–\(\text{O}^{-}\) for determination of stoichiometry. Then, although corundum is \(\text{Al}^{3+}\text{O}_2^{-}\), the interfacial layer is expected to be \(\text{Al}^{3+}\text{O}_3^{-}\). In order to assess the relative stability of this stoichiometry, we have also examined \(\text{AlO}_2\) and \(\text{Al}_2\text{O}_3\) arrangements. In the following we present data relating to structure, energy and EA for (001) and (111) diamond surfaces.

The underlying surface geometry and periodicity plays a significant role in the arrangement of Al on an O-terminated surface in terms of obtaining the desired stoichiometry. We start with arrangements with an O:Al ratio of 3.

1. \(\text{AlO}_3\)

We start with the (001)-surface (Figure 2(a)), where each surface site has been terminated by an oxygen atom. High-symmetry sites on the surface have been labeled\textsuperscript{43,44}. Figure 3(a) shows the lowest energy structure obtained, with half the Al atoms at P, and half at C, which results in co-ordination of the Al-ions with four the O-ions, but no Al-Al bonds. A similar structure with Al over reconstructions (P and B sites) is less energetically favorable by 0.3 eV per surface C-atom. Addition of all Al at P-sites means they each co-ordinate with four oxygen atoms, but also form Al-Al bonds.

We have also examined (001) surfaces with structures where surface oxygen are not all co-ordinated with Al, with illustrations in Fig. 4 representative of ether and ketone bonding, the the ketone structuring being only barely metastable, rearranging into the ether form following a small displacement of the O atom. The unterminated single and double C–O bond lengths are 1.48 Å and 1.19 Å, respectively, in good agreement with previous theory for O-terminated diamond\textsuperscript{45}. Bare oxygen on the (001)-(2×1) surface does not involve C–C reconstruction. The structures in Fig. 4 have PEAs of 1.0 eV and 1.20 eV for the ether and ketone surfaces respectively. The PEA in these cases reflects the dominance of the PEA of O-terminated diamond\textsuperscript{7} and the reduction of the ionicity of the Al-O groups arising from direct Al–Al interactions. C-O-C bonds are more energetically favorable.
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FIG. 3. AlO$_3$ terminated diamond surfaces. (a) (001)-(2×1), (b) (111)-(1×1), and (c) (111)-(2×1). Lengths in Å. Red, light-gray, and dark-gray spheres represent O, Al, and C, respectively. Schematics are viewed approximately along the [110] direction.

by 29 meV per surface site than Fig 4(a), and overall the ketone-structure is less energetically favourable than the (001)-(2×1) model in Figure 3 by 0.1 eV per surface site. Where the AlO$_3$ terminated surface is partially terminated by bare O sites, direct Al–Al interactions are more evident: Fig. 3 illustrates Al–Al inter-nuclear distances of 2.53 Å, 12% shorter than those in Al metal (2.86 Å).

We next turn to the (111)-(1×1) surface. In the absence of reconstruction, the termination of the surface sites by oxygen yields C–O bonds pointing directly away from the surface. We examined a range of arrangements of Al on this surface, with the lowest energy we found being illustrated in Figure 3(b). The Al locate at alternating sites, equidistant from three O-sites, forming AlO$_3$ islands covering the surface, with the Al ions lying 0.44Å further from the diamond than the layer of O-ions. Turning to the (111)-(2×1) reconstructed surface, Fig. 2(b), we have labeled high-symmetry surface sites analogously to the (001)-surface, with the addition of the top (T) site lying directly over a surface site. The lowest energy structure is illustrated in Fig. 3(c), which locates the Al atoms at C-sites, forming islands similar to the (111)-(1×1) surface, but with the [111] displacement of Al ions with respect to some oxygens much smaller at just 0.27Å. Although the reconstruction yields a lower energy in the case of the unterminated diamond, the AlO$_3$ termination, although metastable, is significantly less energetically favorable than the (1×1) case.

Table II lists the calculated adsorption energies and EAs for the three surfaces terminated with AlO$_3$. We find a relatively large NEA of 2.1 eV and adsorption en-

FIG. 4. Example AlO$_3$ terminated (001)-(2×1) surfaces exhibiting (a) ketone and (b) ether configurations. Colors and directions are as in Fig. 3.
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FIG. 5. Electronic band structures of the (111)-(1\times1) surface for (a) Al\textsubscript{2}O\textsubscript{3}, (b) Al\textsubscript{2}O\textsubscript{2}, and (c) Al\textsubscript{2}O\textsubscript{3} stoichiometries, along high symmetry branches of the two dimensional, orthorhombic surface Brillouin zone. The labels for the k-axis follows the conventional definitions\textsuperscript{47}. The energy scale is defined so that zero is the valence band maximum of bulk diamond and the fermi energy of the specified structure. Only bands in the vicinity of the band-gap are shown. Occupied and empty bands are shown in blue and red, respectively.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>(001)-(2\times1)</th>
<th>(111)-(1\times1)</th>
<th>(111)-(2\times1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA</td>
<td>-2.1</td>
<td>-3.4</td>
<td>-2.3</td>
</tr>
<tr>
<td>E\textsubscript{ads}</td>
<td>-0.90</td>
<td>-0.97</td>
<td>-0.17</td>
</tr>
<tr>
<td>O–Al Z\textsubscript{disp}</td>
<td>0.2–0.3</td>
<td>0.4</td>
<td>0.1–0.3</td>
</tr>
</tbody>
</table>

TABLE II. Calculated EAs (eV), formation energies (eV per diamond surface site), and O–Al displacement in the surface-normal direction (\AA) for Al\textsubscript{2}O\textsubscript{3} termination.

For the most energetically favorable Al\textsubscript{2}O\textsubscript{3} terminated surface, the band structure is presented in Fig. 5(a). The underlying diamond valance and conduction bands are highlighted, identifying degenerate, unoccupied surface states around 0.0–1.0 eV above the valence band. The overlapping is indicative of the surface being metallic.

2. Al\textsubscript{2}O\textsubscript{2}

We next turn termination of the diamond surfaces with an O:Al ratio of 2.

TABLE III. Calculated EAs (eV), formation energies (eV per diamond surface site), and O–Al displacement in the surface-normal direction (\AA) for Al\textsubscript{2}O\textsubscript{2} termination.

<table>
<thead>
<tr>
<th>Energy (eV)</th>
<th>(001)-(2\times1)</th>
<th>(111)-(1\times1)</th>
<th>(111)-(2\times1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA</td>
<td>+1.0</td>
<td>-0.1</td>
<td>-0.3</td>
</tr>
<tr>
<td>E\textsubscript{ads}</td>
<td>-0.05</td>
<td>-0.05</td>
<td>+1.21</td>
</tr>
<tr>
<td>O–Al Z\textsubscript{surf}</td>
<td>0.7</td>
<td>0.9</td>
<td>0.7–1.0</td>
</tr>
</tbody>
</table>

For the most energetically favorable Al\textsubscript{2}O\textsubscript{3} terminated surface, the band structure is presented in Fig. 5(a). The underlying diamond valance and conduction bands are highlighted, identifying degenerate, unoccupied surface states around 0.0–1.0 eV above the valence band. The overlapping is indicative of the surface being metallic. These have been examined for their localisation and they are clearly vacuum states, analogous the those presented in the Squeetal. paper\textsuperscript{45}. This state is indicative of incompletely ionized Al. The relatively simple band structure reflects the overall fully bonded nature of the Al\textsubscript{2}O\textsubscript{3} termination, and helps explain the relative stability of this termination.

As the Al:O ratio increases, there are proportionately fewer anions to offset the Al cations. The resulting structures include Al–Al neighbors, and we find that the formation become less energetically favorable (Table III). Upon examination of the band structure, we find Al\textsubscript{2}O\textsubscript{2} termination is metallic and a marked increase in the surface normal distance (Fig. 6); normal displacements are 0.2–0.4 \AA\ for Al\textsubscript{2}O\textsubscript{3}, and range between 0.7 and 1.0 \AA\ for Al\textsubscript{2}O\textsubscript{2}. Al–Al distances (Fig. 6(a)) are similar to those of Al\textsubscript{2}O\textsubscript{3} surfaces containing unterminated O-sites (Fig. 4) at around 2.50 \AA. In addition to the reduction in adsorption energy, there is a decrease in the charge polarisation, making the EA less negative (Table ??), and in the (001) surface, changing it to a PEA.

Fig. 5(b) illustrates the effect of an increasing Al areal-density upon the band structure, with a clearly metallic
behavior. The states lying around the Fermi energy are characterized by ???. If such surface terminations were to be formed, they would be expected to contribute to a surface conductive channel.

3. $\text{Al}_2\text{O}_3$

We have also examined termination by the bulk $\text{Al}_2\text{O}_3$ stoichiometry. We find that $\text{Al}_2\text{O}_3$ terminated surfaces are relatively energetically unstable and generally exhibit PEAs (Table IV). Figure 7 shows examples of the complex bonding networks typical for this Al:O ratio. Although most structures contain Al–Al bonds, Fig. 7(c) shows a (111) oriented structure with only Al–O and

TABLE IV. Calculated EAs (eV), formation energies (eV per diamond surface site), and O–Al displacement in the surface-normal direction (Å) for $\text{Al}_2\text{O}_3$ termination.

<table>
<thead>
<tr>
<th></th>
<th>(001)-(2×1)</th>
<th>(111)-(1×1)</th>
<th>(111)-(2×1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EA</td>
<td>+1.0</td>
<td>+1.0</td>
<td>+1.2</td>
</tr>
<tr>
<td>$E_{\text{ads}}$</td>
<td>+1.45</td>
<td>+1.63</td>
<td>+2.76</td>
</tr>
<tr>
<td>O–Al $Z_{\text{surf}}$</td>
<td>0.7–1.4</td>
<td>1.1</td>
<td>0.4–1.0</td>
</tr>
</tbody>
</table>
C–O bonding. Nevertheless, this structure yields the largest calculated PEA (1.18 eV), indicating that the relative partial charges are unfavorable for a NEA. Figure 7 also illustrates Al–O and C–O bond lengths of 1.78–1.89 Å and 1.38–1.41 Å, respectively. The relatively wide range of distances is correlated with the low-symmetry structures with non-equivalent O and Al species. Some Al–O bond lengths are larger than in bulk Al₂O₃, suggesting a weaker interaction, consistent with the imbalance in anions and cations.

IV. Conclusions

Density-functional simulations of the effects of surface arrangement and stoichiometry of aluminium oxide on the (111) and (001) diamond surfaces have determined the stability and electron affinity for a range of Al:O ratios. Generally, diamond–O–Al arrangements are more stable, wherein the oxygen may be considered to be in the −1 oxidation state. This in turn yields a stoichiometric monolayer with an AlO₃ composition. With this ratio of terminating species, we predict a large NEA, estimated at −3 eV. The thermal stability, as judged by the exothermic reaction between the untermatined diamond and bulk Al₂O₃, suggests that such monolayer terminations would be viable for electron emission and related applications up to much higher temperatures than for other terminations such as copper, cesium, lithium and their respective oxides.

We also find that higher Al:O ratios of 50% and 67% result in a marked decrease in energetic stability and severely reduced NEAs or even PEAs. However, since the most stable termination is that with the most favorable NEA, it seems plausible that even if a mixed termination is realized experimentally, careful control over the deposition conditions is expected to result in viable surface treatments. For example, the most stable Al₂O₃ monolayer termination results in a very Al-rich surface, and it would be these Al atoms that will be most susceptible to desorption.

V. Acknowledgements

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P. K. Baumann and R. J. Nemanich. Electron affinity and


M. J. Rayson and P. R. Briddon. Highly efficient


