Thermal stability and oxidation of group IV terminated (100) diamond surfaces

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High resolution x-ray photoelectron spectroscopy was used to explore the thermal stability of as-prepared and oxidised silicon and germanium-terminated (100) diamond surfaces which form two domain (3×1) surface reconstructions. The as-prepared germanium and silicon-terminated surfaces are stable up to 1200, making them the most thermally stable surface termination for diamond (100). The oxidised forms of these surfaces can be created via exposure to O$_2$, H$_2$O or atmospheric conditions and retain the (3×1) surface symmetry. The thermal stability of the oxidised surfaces exhibit differing behaviour. A 700°C anneal is sufficient to liberate oxygen from the germanium-oxide terminated (100) diamond surface, leaving the pristine germanium-terminated surface, while the silicon-oxide terminated surface is thermally stable up to 1200°C, at which point both silicon and oxygen are removed.

1 Introduction Functionalised diamond surfaces have emerged as a promising device platform in many diverse application areas, such as high sensitivity nanomagnetometry [1, 2], biosensing [3-5], cold cathode electron emitters [6-8] and spintronics [9-12]. The interest in diamond surfaces stems from the ability to engineer significantly contrasting properties with a simple change in the terminating species, as well as the advantages that bulk diamond properties offer for such applications. Extending the range of available terminations offers new possibilities for developing diamond surfaces as a technologically relevant platform. Typical elemental terminations include hydrogen [13], oxygen [14], nitrogen [15, 16] and fluorine [17, 18]; more complex terminations based around metal-oxides have been developed [19, 20], as well as biologically relevant organic functionalisations [21]. While the chemically inert nature of diamond is considered a benefit for a large number of applications, Raymakers et al. have shown that forming a covalent surface functionalisation with diamond is complicated by the stability and chemical passivity of the diamond surface [22]. Typical processing steps for terminating diamond surfaces require that the surface be exposed to harsh chemicals, or to radicals created through thermal cracking of molecules or in a plasma. Such treatments have a tendency to etch the surface and yield chemical inhomogeneity. While this does not necessarily impact the utility of diamond surfaces in all applications, the desire for surface-based electronics and subsurface defect center devices creates a need for greater control over the morphology and chemical structure of the diamond surface [10].

1.1 Group IV terminations of (100) diamond We have recently shown that the (100) diamond surface can be terminated with group IV elements, forming silicon-terminated (SiTD) [23] and germanium-terminated (GeTD) (100) diamond [24]. In both cases, the preparation procedure for these surfaces begins with the highly ordered C(100)- (2x1):H surface [25] and then proceeds in a manner which, in principle, should preserve the atomically flat terraces as associated with this surface, while modifying the surface electronic properties. Both the SiTD and GeTD surfaces possess a small negative electron affinity. Low energy electron diffraction (LEED) shows that both terminations cause the surface to transition from the two-domain (2×1) structure associated with the hydrogen-terminated surface, to a two-domain...
(3×1) structure which we believe has the same origin in both cases. Figure 1 shows the alternating monomer-dimer model proposed for the (3×1) reconstruction, derived from the results of synchrotron-based X-ray Photoelectron Spectroscopy (XPS) and LEED characterisation of these surfaces. One feature of the proposed model is that each adatom forms two bonds with the underlying carbon surface and has two dangling bonds associated with it. This structure is supported by studies demonstrating the oxidation of silicon-terminated diamond [25], where chemical modification of the surface-bound silicon is evident, but the (3×1) reconstruction and the carbon chemical states are otherwise preserved.

While the proposed ideal reconstruction for the SiTD and GeTD surfaces is identical, in practice there are key differences. Importantly, while a completely silicon-terminated (100) diamond surface can be readily prepared [23], germanium-terminated surfaces have been prepared with a germanium coverage only up to 0.63 ML [24]. This limitation appears to be derived from steric hinderance due to the larger atomic size of germanium compared to silicon, rather than any kinetic barrier limiting the extent of the bonding reaction. This may limit the use of germanium terminated diamond in applications where surface homogeneity is critical. However, the group IV terminations of diamond have more to offer than simply the properties of their pristine as-prepared surfaces. For example, we have recently shown that when oxidised, SiTD can be p-type surface transfer doped with an adlayer of MoO$_3$ [26], in a similar fashion to hydrogen-terminated diamond [27, 28]. While forming a material interface with diamond may be difficult due to the conditions typically required for chemical functionalisation, silicon and germanium have a rich variety of functionalisation schemes [29, 30] and well-established fabrication protocols which may now be applicable to diamond through this Si or Ge bridging layer, fostering even greater tunability in the properties of the diamond surface. This may include the possibility to functionalise the surface with optically active or magnetic species.

The present work focuses on understanding aspects of Group IV terminated diamond which are relevant to integrating the Si and Ge terminated surfaces into real device systems. As a complimentary study to our previous work exploring the oxidation of SiTD [25], we explore the behaviour of GeTD when exposed to sources of oxygen, specifically H$_2$O and O$_2$ dosed under ultra high vacuum (UHV) conditions, as well as full atmospheric exposure. As in the case of the oxidation of SiTD, the germanium oxidises in all three cases while the carbon-germanium bonding and (3×1) surface reconstruction are retained. The thermal stability of pristine SiTD and GeTD, as well as the oxidised form of these surfaces, is examined. The ability to anneal diamond samples without disturbing the surface has relevance to developing device architectures based on Group IV terminated surfaces, both because this may influence the processing steps which are compatible with these terminations and as the activation rate of bulk dopants is correlated with temperature. A crucial factor, then, is determining the temperature to which our group IV terminations are stable. We show that the pristine surfaces are stable up to 1200°C when annealed under UHV conditions, considerably higher than for the hydrogen-terminated (100) diamond surface [13, 31, 32], where the hydrogen is removed with a 950°C anneal, leaving a highly reactive bare surface which furthermore begins to graphitise at 1200 [33]. The oxidised surfaces present differing behaviour. Oxygen desorbs from oxidised GeTD with a 700°C anneal, reverting to the pristine germanium-terminated surface. In contrast, oxidised SiTD is stable to 1200°C, at which point the oxygen desorbs, liberating...
silicon from the surface with it. As shall be explored, this contrasting behaviour is attributed to the relative strengths of the Ge-C, Ge-O, Si-C and Si-O bonds.

2 Experimental Details For the measurements presented in this work, each sample is a CVD-grown type-IIa single crystal (100) oriented substrate (Element Six) onto which a (100) oriented boron doped overlayer (B concentration in the range $1\times10^{16} - 1\times10^{18}$ B/cm-$3$) was grown at the Melbourne Centre for Nanofabrication (MCN), to prevent charging in the course of measurements. Scanning Tunneling Microscopy studies have been performed to show that the grown overlayers possess atomically flat terraces with a terrace width of typically 30 nm [13].

2.1 Preparation of pristine Group IV terminated surfaces Our preparation methods for the silicon [23] and germanium [24] terminated surfaces are reported in extensive detail elsewhere, and we summarise the key points here for the benefit of the reader.

The starting point of our preparation is a (100) oriented substrate which has been hydrogen-terminated by exposing the substrate to a microwave hydrogen plasma, such that it forms the well-known two-domain (2×1) reconstruction [13]. Following hydrogen termination, the selected substrate is loaded into a UHV environment where it is annealed at 450°C for at least 30 minutes to remove atmospheric contamination, and it is in this UHV environment that all subsequent preparation is performed. From this point, three processes must occur to successfully terminate the (100) diamond surface:

- Deposition of sufficient adlayer material (silicon or germanium) to satisfy the reconstructed unit cell
- Removal of hydrogen (achieved by annealing the sample to 950°C [31, 32])
- High temperature annealing to form the (3×1) reconstruction

To achieve these goals, silicon or germanium is evaporated under UHV conditions, with a pressure no higher than $5\times10^{-10}$ mbar during deposition. The silicon is evaporated by passing a DC current through a rectangular piece of silicon wafer (approximately 25 mm x 4 mm) until the temperature is sufficient to cause evaporation. Germanium is deposited using a commercial effusion cell (HTZ cell, MBE Komponenten) equipped with a graphite crucible. In each case, the source is positioned approximately 30 cm from the sample.

Our model of the (3×1) surface contains two adatoms per surface supercell. That amounts to an atomic density of $1.048\times10^{15}$ cm$^{-2}$. Using a calculation of photoelectron attenuation we correlate this adatom density with a measurable ratio of XPS peak intensities, and use this metric to determine our coverages.

On the silicon terminated surface, excess deposited material cannot be removed, thus we aim for exactly 1 ML, whereas we have found that excess germanium will desorb during the annealing step, so we deposit in excess of 1 ML in order to maximize terminated coverage.

The samples were then annealed using an electron-beam heater incorporated in the sample plate for the removal of hydrogen and the surface reconstruction. The sample holder and deposition stage were thoroughly outgassed before the sample holder was removed from vacuum and the sample mounted. This was to mitigate as far as possible the evolution of
oxygen during sample preparation, to maximize the quality of the pristine samples.

As we describe elsewhere [24], there is some flexibility in the order and implementation of these steps. The most commonly used process has been to deposit the desired material onto the hydrogen-terminated diamond surface, then to anneal the substrate to 950 °C for 30 minutes. This anneal simultaneously both desorbs the hydrogen from the surface and enables the reaction and relaxation necessary to form the (3×1) reconstruction [23, 24]. As an alternative, we have also found that a high quality termination can also be achieved by annealing the sample to remove the surface hydrogen, then depositing material and finally annealing again for the surface to relax into the (3×1) reconstruction. Furthermore, while annealing at temperatures lower than 950°C will result in bonding between the adatom and the diamond (100) surface, we find that annealing at 950°C is required to produce a completely reconstructed surface [24].

2.2 Surface characterisation and oxidation Measurements were performed at the Soft X-ray Spectroscopy (SXR) beamline of the Australian Synchrotron. The beamline end-station is equipped with a SPECS Phoibos 150 hemispherical analyser, leak valves for controlled gas dosing and a reverse-optics LEED system for monitoring the surface reconstruction. The samples were mounted inside a Ta envelope on a sample holder with an underlying electron beam heater, enabling annealing to temperatures of 1200°C reproducibly. A K-type thermocouple in direct contact with the sample envelope and an optical pyrometer were simultaneously used to monitor the sample temperature during annealing steps. All measurements were performed at pressures below 5×10⁻¹⁰ mbar.

The samples were exposed to molecular H₂O and O₂ using a precision leak valve for controlled dosing. During exposure, the dose (in Langmuirs, L) was estimated by monitoring the partial pressure of the species using a residual gas analyser (Stanford Research Systems RGA 300). The recorded partial pressure curve was integrated following each exposure to precisely determine the administered dose.

High resolution XPS measurements of the C1s, Si2p and Ge3d core levels were performed using the photon energies listed in Table 1. In each case the photoelectron kinetic energy falls within the range 50-70 eV, maximising the surface sensitivity of these measurements. In addition, XPS survey scans were acquired to evaluate surface cleanliness using a photon energy of 850 eV. The binding energy (BE) scale of all XPS spectra were referenced to the Fermi level either by setting the Au4f7/2 core-level BE to 84.00 eV (for C1s spectra) or by monitoring the Fermi edge of a gold foil in electrical contact with the sample (for Si2p and Ge3d spectra). Core level spectra were fitted using Voigt components with the Lorentzian widths listed in Table 1, after first applying a Shirley background correction [36].

For the doublet Si2p core level, the spin-orbit split components of the Si2p₁/₂ and Si2p₃/₂ components have been constrained to have a binding energy separation of 0.6 eV and the required branching ratio of 0.5. For the doublet Ge3d core level, the Ge3d₃/₂ and Ge3d₅/₂ have a binding energy separation of 0.59 eV and branching ratio of 0.67. The relative and absolute binding energy uncertainties of our measurements are estimated as 0.05 eV and 0.1 eV for the Si2p and Ge3d core levels, respectively. For clarity, fitted core-level spectra illustrated in this paper show the Si2p₁/₂ and Ge3d₃/₂ components in transparency[24,35].
3 Results and Discussion

3.1 Thermal stability of pristine Si and Ge-terminated (100) diamond

Silicon and germanium terminated surfaces were prepared using the process described above and characterised after cooling to room temperature and after a subsequent annealing step at higher temperature (1200°C) to test whether these surfaces are stable to temperatures higher than the 950°C reconstruction temperature.

Figure 2 shows the C1s and Si2p core levels of SiTD, before and after a 1200°C anneal for 15 minutes. The surface related components of both the Si2p and C1s core levels have narrowed, leading to a sharpening of the spectral features. This may be qualitatively interpreted as an improvement in the quality of the reconstruction as a result of the high temperature treatment. Furthermore, a small amount of surface oxygen which was present following the initial preparation of the terminated surface, as evident in the O1s core level (inset) was removed during the 1200°C anneal, further showing an improvement in the surface quality. For the case of the germanium-terminated surface, shown in Figure 3, the changes to the core level structure are more complex yet support a similar conclusion. As noted above, we have found that the maximum achievable germanium coverage on the germanium-terminated surface is approximately 0.63 ML [24]. As a result, some of the surface-related components are in part attributed to those unit cells which are “incomplete”; these are indicated in Fig. 3. Following an anneal of 1200°C, we observe a relative decrease in the component C1, which is attributed to sites in incomplete unit cells, accompanied by a relative increase in the C2 and C3 components which have been attributed to surface carbon atoms bonded to, respectively, one and two germanium atoms [24]. Concurrently, there is a relative decrease in the bulk-like component of the Ge3d spectrum (Fig. 3, right). In short, there are subtle changes which qualitatively reflect some improvement in the surface, but more importantly we do not observe any new indications that a high temperature treatment has removed any of the surface-bound germanium or caused the formation of any new components. Thus, our measurements indicate that annealing to 1200°C has little impact on the as-prepared pristine silicon- and germanium-terminated (100) diamond surfaces, other than to perhaps improve the quality of the surface reconstruction in both cases.

3.2 Oxidation of Ge-terminated (100) diamond

We have previously explored the oxidation of the silicon terminated (100) diamond surface [25], and turn now to the behaviour of the germanium-terminated surface upon exposure to sources of oxygen. Figure 4 shows the Ge3d and C1s core levels of an as-prepared germanium-terminated (100) diamond surface for reference, along with the same core levels for surfaces subsequently exposed to O2 (RGA integrated total exposure: 10852 L), H2O (RGA integrated total exposure 7128 L), and atmosphere (10 minutes, i.e. approx. 1011 L exposure to O2 and 1010 L exposure to H2O). The Ge3d spectrum for the as-prepared surface is dominated by a peak assigned to the pristine germanium-carbon termination (labelled GeC in the figure), with a smaller feature at lower binding energy attributed to excess germanium remaining on the surface after the initial preparation, as described in detail elsewhere [24]. We observe two changes in the Ge3d spectra that are attributed to oxidation. Firstly, the O2 and H2O dosed samples show a single additional component (labelled G1 in the figure) to high binding energy of the component GeC.
Our fit for this new component is based on systematic fitting of spectra from these three samples, resulting in a core level shift of 0.85±0.05 eV relative to the GeC component; the component positions are shown in Table 2. We attribute this component G1 to germanium which is bonded to a single oxygen atom, in addition to the underlying carbon lattice. Turning to the the atmosphere exposed sample, we find that the Ge3d spectrum is composed of three components. Two of these are attributed to the same GeC and GeO species as in the case of the O2 and H2O exposed surfaces, with the GeO component (G1) shifted in binding energy by 0.86 eV relative to GeC. The third component (Ge2) appears at a core level shift of 1.65 eV relative to GeC and is assigned to GeO2. For the atmosphere exposed sample, the measured Ge3d component shifts of 0.86 eV and 1.65 eV relative to GeC in both cases represent a shift of roughly half that seen in work on bulk germanium [37]. However, Kuhr and Ranke [38] describe a variation in chemical shift of Ge1+ across a range 0.56 to 1.17 eV, and Ge2+ across a range 1.72 to 2.03 eV, dependent on crystal orientation. Given these reported ranges, and the reduced induction effect due to the bonding of the Ge atom to the underlying (higher electronegativity) carbon lattice in this system, we are confident in the assignment of these peaks as described above.

In contrast to the oxidation of SiTD surfaces, the adsorption rate of oxygen containing species on the GeTD surface was observed to be very low. The GeO component, in the maximally exposed H2O (O2) sample represents only 20% (34%) of the core level. In contrast, exposure to just 1170 L of H2O was previously shown to result in almost 50% oxidation of the SiTD surface [25]. Even in the case of the atmosphere-exposed GeTD surface, the sum of both oxide species present in Figure 4 still represents only 85% of the total core level intensity. Our previous study of the oxidation of SiTD showed that the exposure to atmosphere resulted in not just near-total oxidation, but near-total conversion to the Si2+ oxidised state. In contrast, here the Ge2+ core level intensity is found to represent just 31% of the Ge3d core level spectrum for the atmosphere exposed surface. These results are in agreement both with the oxidation behaviour described for bulk Ge [37], where a significant formation of GeO2 was only observed after exposure to atmosphere, and with measurements of the adsorption of water on bulk Ge [39] which showed that the sticking coefficient of water on germanium is quite low at room temperature, an effect which is apparently not mitigated in our system despite the known reactivity of dangling bonds. In bulk germanium, the low rate of GeO2 formation by oxidant exposure in vacuum is attributed to the similar stability of GeO and GeO2, whereas SiO2 is significantly more stable than SiO [40]. This difference is a reasonable explanation for the contrasting behaviour we observed between these two Group IV terminations of diamond.

We now turn to a brief discussion of the C1s core level corresponding to each of the three oxidized GeTD samples. These are shown in Figure 4, along with the corresponding core level for the as-prepared surface. As noted above, the germanium termination achieves a maximum coverage below 1 ML, and thus it is reasonable to consider whether the surface carbon which has not bonded with germanium remains vulnerable to oxidation. Oxidation of the bare (100) diamond surface generates C1s components to high binding energy of the bulk diamond peak [20, 33]. For the C1s spectra shown in Figure 4, while there is some change in the distribution of spectral weight to the high binding energy side of the bulk diamond component, we do not attribute this to the oxidation of surface carbon based on the following argument. We have employed the same five component model in fitting the C1s core levels of both the clean GeTD
C1s and those of the oxidised samples. The component to higher binding energy of the bulk component in this five component model (labelled B* in Figure 4, as in our previous work [13, 34]), makes up 15% of the bulk core level and is associated with near-surface atoms which experience a final-state shift [13]. Since the magnitude of this final-state shift and the width of this component are dependent on a number of complex factors, including the surface dielectric constant, it is expected that this peak will change with surface oxidation in a manner which cannot currently be predicted. As a result, we cannot rule out that this component may mask features related to slight oxidation of the surface. However, Maier et al. [33] describe a chemical shift of 2.5 eV to higher binding energy of the bulk peak for the C-O component, well beyond the range of the B* component employed in the present work; thus we state with some confidence that the surface is not oxidized to a meaningful extent. That oxidation of the surface carbon which is not bound to germanium is not observed may be interpreted as further support for our hypothesis that 63% represents a maximum surface layer packing, and sufficiently shields the surface carbon atoms from further bonding.

As a final point in the characterisation of the oxidised GeTD surface, we consider whether oxidation affects the two domain (3×1) reconstruction which is unique to the Group IV terminations. In previous work we showed that exposing the SiTD surface to oxidation sources causes the formation of (C-)SiO and (C-)SiO2 related components in XPS, while retaining the characteristic (3×1) surface structure seen in LEED. Here we report this to be similarly true for the oxidation of germanium-terminated (100) diamond. Figure 5 shows the LEED patterns for Si, SiO, Ge and GeO terminations. In both the Si and Ge cases, oxidation causes an increase in the diffuse background signal, while the (3×1) symmetry is retained.

3.3 Thermal stability of oxidised Si and Ge-terminated (100) diamond

In order to determine the thermal stability of the oxidised surfaces, the samples were annealed to increasingly higher temperatures until a change in the survey spectra, measured at room temperature after each anneal step, was observed. Here follows the results of annealing on three representative samples.

The first two samples were Ge terminated; the corresponding Ge3d core level spectra of the GeTD surfaces are shown in Figures 6(a) and 6(d). The two surfaces have the same Ge coverage (0.73 ML). For the case of Figure 6(a) a slightly higher bulk Ge component relative to the surface component is evident (0.15, compared to 0.13 in the case of Figure 6(b)) and the Gaussian widths of the surface components are also slightly higher in Figure 6(a) (0.64 eV compared to 0.59 eV), which is ascribed to a more inhomogeneous sample. This explains the slightly different spectra for the two as-prepared samples, however these factors do not affect the present study.

For the first sample investigated, the GeTD surface was exposed to 10kL of O2, giving a GeO component of 34% of the total Ge3d core level intensity. This sample was annealed for 15 minutes at 700°C; the effect on the Ge3d core level is shown in Fig. 5 (a) to (c), where a clear similarity between the pre-oxidised and post-anneal core levels is observed. The post-anneal fit includes a GeO component comprising 3.5% of the core level, or about 10% of the amount of pre-anneal oxidation. For the second sample, the GeTD surface was exposed to 7kL of H2O, giving a GeO component only 20% of the Ge3d core level intensity. We noted, in the previous
section, the relatively poor adsorption of water onto the germanium terminated surface. Furthermore, it was observed in [39] that adsorbed H₂O dissociates into atomic oxygen at 450K. This sample was annealed to 300°C, for which the effect on the Ge3d core level is shown in Fig 5 (d) to (f). That low temperature annealing was apparently sufficient to cause the complete desorption of oxygen from the surface and conversion of (C-)GeO back to GeC. In this case, we did not need any GeO component to fit the core level. The relatively easy reversal of the oxidation of the germanium termination via low temperature annealing is contrasted now with the higher temperatures required to reverse the oxidation of the SiTD surface.

The C1s and Si2p spectra for the as-prepared, oxidised and annealed SiTD surface are shown in Figure 7. The as-prepared Si2p core level was fit with two components, at 99.55 eV and 100.63 eV, which account for 81.4% and 19.6% of the core level intensity respectively. As the ratio of oxygen to carbon as indicated by survey scan (also shown) is less than 1%, we attribute the higher binding energy component to step edge bonded silicon, which has a higher carbon co-ordination than the ideal termination. This sample was heavily oxidized in UHV by O₂ exposure, such that no unoxidized component was required for fitting; the core level consisted of 56% Si^{1+} (100.92 eV) and 44% Si^{2+} (102.22 eV). The corresponding growth of the O1s peak in the survey scan (approx. 530 eV) is illustrated in Figure 7 (c). After oxidation, the O1s to C1s peak ratio had increased to 28%. The C1s core level is broadened and structure is lost, however it may still be fit using the four peak model of the as-prepared surface, with broadening attributed to scattering from the oxygen overlayer.

Due to the higher annealing temperatures required for the case of SiTD, the sample was flash annealed four times; that is, it was rapidly ramped to the temperature set point, held for 10 seconds, and then ramped down to room temperature over a period of 1 minute. The sample was flashed to 1200°C twice, causing a reduction in oxygen ratio to 17% in the survey scan. It was then flashed twice to 1400°C, reducing the oxygen to carbon ratio to below 1%. The Si2p core level resulting from this annealing is shown in Fig. 7 (b). Evident in this spectrum is a return to the chemical composition of the pristine SiTD surface, in this case the SiC component accounting for 81.5% and Si^{1+} for 18.5%, similar to the pre-oxidation composition. However, it is also important to consider whether silicon is removed by this process. If we quantify the silicon coverage before and after thermal treatment, using the attenuation method we have used in previous work [23], we find that the coverage has gone from 1.44 ML pre-anneal to 0.73 ML after the flashing, a loss of about half the Si. As this is accompanied by a complete loss of the surface oxygen, we attribute this to desorption of silicon as a silicon-oxide moiety, although at this stage have no specific knowledge of the mechanism involved [41, 42]. While silicon remains on the surface, we cannot claim to have shown that the pristine termination would be resistant to 1400°C flashing. However, we do observe that surface silicon-carbon bonds are capable of resisting this treatment, and that the (3×1) termination is similarly resilient, as may be seen in Figure 7 (d).

4 Conclusion This article has presented data showing the oxidation of the germanium-terminated (100) diamond surface and the thermal stability of pristine Group IV terminated (100) diamond surfaces, as well as the oxidised variants of those surfaces. The pristine GeTD surface is shown to be vulnerable to oxidation from H₂O and O₂ in vacuo, and will
oxidise on exposure to atmospheric conditions. However, the GeTD surface may be less vulnerable to oxidation when compared to SiTD \[25\], as atmosphere exposure for 10 minutes still leaves 15\% of the surface germanium unoxidised, in comparison to SiTD where the surface has been shown to be near-completely oxidised after the same exposure. While the pristine GeTD surface has been found to reach a maximum coverage of 0.63 ML and thus some surface carbon should be exposed, we note that exposure to oxygen does not oxidise these surface carbon sites, a finding attributed to steric hindrance preventing oxygen from bonding to these sites.

When investigating the thermal stability of these surfaces, the pristine SiTD and GeTD surfaces are found to be stable up to at least 1200°C. Given that the hydrogen desorbs from the hydrogen terminated (100) diamond surface at 950°C \[13, 31, 32\] and the bare (100) surface graphitises at 1200°C \[33\], this shows that these Group IV terminated surface improve the stability of the diamond (100) surface. Such high temperature annealing may be advantageous for optimising the properties of nitrogen-vacancy centers \[43\] and boron doped layers \[44, 45\] in bulk diamond, or useful in enabling higher temperature treatment of near-surface dopant layers. The oxidised SiTD and GeTD surfaces show differing behaviour. It has been observed that an oxidised GeTD surface can be reverted to an as-prepared GeTD surface with an anneal of 700°C, with some species removed at 300. In contrast, the oxidised SiTD surface is stable up to 1200°C, at which point some oxygen species are removed; a heat treatment of 1400°C removes the oxygen completely but also results in removal of some surface silicon.

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**References**


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TABLES

Table 1: The photon energies ($\hbar\omega$) used for measuring high-resolution, surface sensitive core level spectra in the current work and the Lorentzian widths ($w_L$) used during peak fitting analysis of the respective core levels.

<table>
<thead>
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<th>Core level</th>
<th>$\hbar\omega$ (eV)</th>
<th>$w_L$ (eV)</th>
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<tbody>
<tr>
<td>C1s</td>
<td>350</td>
<td>0.15 [32]</td>
</tr>
<tr>
<td>Si2p</td>
<td>150</td>
<td>0.055 [34]</td>
</tr>
<tr>
<td>Ge3d</td>
<td>100</td>
<td>0.17 [35]</td>
</tr>
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</table>

Table 2: Binding energy positions (in eV) and assignments of the Ge3d$_{5/2}$ components in the spectra shown in Figure 4.

<table>
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<tr>
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<th>GeO</th>
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<td>Clean</td>
<td>28.90</td>
<td>29.26</td>
<td></td>
<td></td>
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<tr>
<td>H$_2$O</td>
<td></td>
<td>29.27</td>
<td>30.08</td>
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<tr>
<td>O$_2$</td>
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<td>30.50</td>
<td></td>
</tr>
<tr>
<td>Atmosphere</td>
<td>29.67</td>
<td>30.52</td>
<td>31.32</td>
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FIGURES CAPTIONS
Figure 1: Schematic model with unit cell outlined, C1s x-ray photoelectron spectra (h\(\omega\) = 350 eV) and LEED pattern for the (2×1) hydrogen terminated (a-c) and (3×1) silicon-terminated (d-f) diamond surfaces.

Figure 2: Fitted C1s and Si2p core level spectra obtained for a silicon-terminated diamond surface, (i) as-prepared and (ii) after a subsequent 1200°C anneal. Components are vertically offset from the spectra, and only the Si2p\(_{3/2}\) components are displayed, for clarity. Inset shows the corresponding O1s core level from a survey scan.
Figure 3: Fitted C1s and Ge3d core level spectra for a germanium-terminated diamond surface, as-prepared (bottom) and after a subsequent 1200°C anneal (top). Components are vertically offset from the spectra, and only the Ge3d_{5/2} components are displayed, for clarity.

Figure 4: Germanium-terminated (100) diamond before (Pristine) and after exposure to H₂O or O₂ in situ, and exposure to atmospheric conditions. Components are vertically offset from the spectra, and only the Ge3d_{5/2} components are displayed, for clarity.
Figure 5: LEED patterns for pristine and oxidised Group IV terminated diamond surfaces. The rotation of the oxidised GeTD pattern relative to the pristine GeTD pattern is the result of remounting the sample after atmosphere exposure.

Figure 6: Ge3d spectra illustrating the thermal stability of the oxidized GeTD surface. (a,d) Pristine; exposed to (b) 10kL O$_2$, (e) 7kL H$_2$O; subsequently annealed for 15 minutes to (c) 700°C, (f) 300°C.
Figure 7: C1s (a) and Si2p (b) core level spectra demonstrating the thermal stability of the oxidized SiTD surface. Survey scans (c) show the clean (i), oxidized (ii), after being flashed twice at 1200°C (iii), and finally after two further flashes at 1400°C (iv); (d) LEED patterns corresponding to the pristine and post-treatments surface.
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