THE OXIDATION OF DIAMOND

J.Y. Howe\(^*\), L.E. Jones, and A.N. Cormack

School of Ceramic Engineering and Materials Science
Alfred University, Alfred, NY 14802

Introduction

There is a renewed interest in the oxidation of diamond because of the development and application of diamond-based electronic devices. Diamond oxidation and phase transition are connected phenomena, yet they are not well understood. Identifying surface active sites, activity of specific crystallographic facets, and the extent to which surface conversion is involved in the oxidation process is key to the fabrication and design of diamond materials.

The carbon atom in its ground state has a 1s\(^2\)2s\(^2\)2p\(^2\) electronic configuration. In diamond, the four valence electrons hybridize and adopt an sp\(^3\) configuration in which all four electrons have the same energy. Carbon and graphite materials have an sp\(^2\) hybridization. A phase transition in diamond may occur when the electronic configuration associated with surface atoms changes from sp\(^3\) to sp\(^2\). Both sp\(^3\) and sp\(^2\) bonded carbons are subject to oxidation at elevated temperatures in-oxygen containing atmospheres. It is well recognized that carbon reacts with oxygen and yields the gaseous products CO and CO\(_2\). However, under debate since the early 1960’s, are the mechanisms associated with diamond oxidation and phase transition of diamond are related still remains controversial and unclear \([1-3]\). A common inadequacy of early diamond oxidation research is the result of underestimating or not considering the phenomena of diamond phase transitions. In many ways, phase transition is an inseparable issue from the oxidation of diamond.

The objective of this work has been to develop a fundamental understanding of the oxidation behavior of diamond. Our research efforts on oxidation and phase transition of diamond are made via experimental and computational approaches. We have shown that our computational simulation results are substantiated by our experimental findings.

Materials and Experimental

CVD diamond film ET100 manufactured by Norton Diamond Film, Northboro, MA, and type 2A natural diamonds with specific cuts, i.e., {111}, {110}, and {100}, from Drukker International, The Netherlands, are the subjects of the research effort. Detailed technical specifications of CVD diamond ET100 can be found elsewhere\([4]\). Highly oriented pyrolytic graphite (HOPG), grade ZYH, manufactured by Union Carbide, and glassy carbon, manufactured by SGL, are the reference materials. HOPG and glassy carbon are chosen simply because they are the crystalline and amorphous carbon materials, respectively, with sp\(^2\) bond character.

CVD diamond ET100 is treated isothermally at high, low, and very low oxygen partial pressures at elevated temperatures. Oxidation at high oxygen partial pressure is carried out using an isothermal gravimetric analysis on a Setaram TAG 24 Thermoanalyzer, in 95 kPa ultrahigh purity O\(_2\) at 693, 773, 823, 848, 873, and 898 K for 30 to 400 min with a flow rate of 70 to 95 sccm. Oxygen treatment at low partial pressure is carried out in the thermal analyzer on the Setaram, at 1023, 1123, 1273, 1573, 1673, and 1773 K. The low oxygen pressures of 0.4 to 18 Pa pO\(_2\) is maintained using a roughing pump. Heat treatments at very low oxygen partial pressure are conducted in flowing titanium-gettered helium using a Stanton-Redcroft (now Rheometric Scientific Inc.) Simultaneous Thermal Analyzer (STA 1500S) at 1276, 1576, and 1741 K for 170 to 600 min. A flow rate of 50 sccm is used for all exposures. Prior to heating, the instrument is purged until the oxygen partial pressure in the exhaust stream lowered to 6 x10\(^{-10}\) Pa, as indicated by a Centorr oxygen analyzer.

Auger spectra are obtained using PHI 680 Auger Nanoprobe. The accelerating potential is 2 kV and the beam current is 1 nA. The ET100 film after heat treatment (in helium flow with an oxygen partial pressure of 6x10\(^{-10}\) Pa at 1741 K for 600 min) is crushed down to small pieces for TEM observation. TEM study is undertaken using a JOEL 2000 FX under 120 kV.

Computational Methodology

\(^*\) Now with Oak Ridge National Laboratory, Oak Ridge TN 37831-6087
Computer simulation is carried out using CASTEP codes on an SGI Octane work station. CASTEP, an acronym for CAmbridge Sequential Total Energy Package, is a commercial software package originally developed by the Theory of Condensed Matter Group at the University of Cambridge, England [5]. It performs total energy calculations that solve quantum mechanical equations for the electronic states of systems containing arbitrary arrangements of atoms using density functional theory. CASTEP calculations are carried out on periodically repeating cells or boxes, usually referred to as “supercells”. The dimension of the supercell may be the same as the unit cell. It can also be set to be larger than the unit cell. Supercells can host not only crystalline species, but also species without periodicity, e.g., an oxygen molecule. The simulation strategy in the current study is to build a supercell with various surface conditions and perform a geometry optimization with respect to the total energy. The cell is built to be large enough to allow relaxation, yet small enough to be computationally economical (smaller cells demand less CPU time, therefore, use fewer computational resources).

Giving as an example, in order to study the surface relaxation and oxygen-chemisorption, a cell of 54 carbon atoms in total is built with six (111) layers; each layer contains 9 carbon atoms, (see Figure 1). There is 10 Å of vacuum on top of the (111) surface. Thus, an infinite 3-D lattice is constructed in a way that it can also be visualized as stacks or slabs (infinite in 2-D) with 10Å of vacuum in between. The vacuum space of 10 Å is large enough to ensure that there are no interactions between adjacent slabs. The (110) and (100) supercells are constructed in a similar manner. These supercells are the templates on which chemisorbed species, mostly oxygen in the current study, can be deliberately added to the top layer. Geometry optimization is then performed on these starting models. The calculations are performed using GGA-PW91 method (general gradient approximation, the Perdew-Wang method) [6, 7]

### Results and Discussions

Although the main Auger peak, carbon KVV, is similar for all the carbon materials, the difference of bond character, sp² vs sp³, can be sought from the first satellite peak in the vicinity of 255 and 265 eV[8-11]. Figure 2 contains the Auger spectra collected from CVD diamond ET100 and glassy carbon. The spectra of diamond treated at 823 K/95 kPa O₂ is quite similar to that of the as-received specimen. The similarity of line shapes between as-received and oxidized diamonds implies that a direct oxidation from sp³-bond carbon without a concurrent phase transition. In contrast, the spectrum of diamond treated at a low oxygen pressure is similar to that of the glassy carbon reference. The lower shoulder at A₁ is the significant feature of sp²-carbon. This clearly shows that after heat treatment at 1741K in 6x10⁻¹⁰ Pa O₂ for 600 min, the surface of diamond changes from sp³ to sp². In other words, oxidation occurs with a phase transition under these conditions.

Figure 1. The diamond (111) supercell used as a template for surface relaxation or chemisorption. The 10Å of vacuum space above the lattice planes simulates the surface of diamond.

![Figure 1](image1.png)

![Figure 2](image2.png)
partial pressure leads to a surface reconstruction to sp² bond character.

Clean Diamond (111) Surface
Clean surface refers to a surface that is free of any adsorbed atoms. Figure 3 is the structure of clean (diamond (111) surface after relaxation created via the computational methodology described. Compared to the starting structure shown in Figure 1, the kinked (111) layers of the sp³ diamond have flattened and the interlayer spacing has increased to 3.40 Å. This structure is chemically analogous to the graphite structure. Simulation studies show that surface reconstruction from sp³ to sp² bonding occurs on clean diamond (111) surface. Experimentally, it is observed upon heat treating CVD diamond film ET100 in low oxygen partial pressures (less than 1 Pa) and temperatures higher than 1123 K, that the surface of diamond becomes black supporting the model’s suggestion that a phase transition to a surface sp² layer occurs. Auger analysis indicates that this black layer possesses an sp² bond character. It is further determined using TEM and electron diffraction that this black layer of carbon is amorphous. Without oxygen, diamond (111) surface reconstructs to amorphous sp²-carbon. However, simulation study indicates that the clean diamond (110) and (100) surfaces still keep retain their sp³ bond character under the same conditions. This indicates that the (110) and (100) surfaces are less subject to surface reconstruction, in other words, more stable.

O-Chemisorbed (111) Surface
Figure 4 is the relaxed diamond (111) with one layer of chemisorbed oxygen. On the supercell described in Figure 1, there are 9 surface sites. A full oxygen coverage refers to that all the sites are covered by chemisorbed oxygen atoms. Fully oxygen-chemisorbed diamond (111) surface maintains sp³ configuration. There is no surface construction on (111) surface.

One might ask what would occur at low oxygen pressures? Our simulation study suggests that diamond (111) surface could convert to an sp² bond character even with the presence of small amount of oxygen, e.g., at low oxygen surface coverage of 11 and 22% (a coverage of 11% is achieved by having one chemisorbed oxygen on surface while 22% coverage is a surface with 2 oxygen atoms.) Figure 5 is the relaxed diamond (111) surface with 22% oxygen coverage. The structure is similar to the clean surface shown in Figure 3. This finding is consistent with the experimental results that diamond experiences a surface phase transition to sp² at oxygen partial pressures ranged from 0.6 to 18 Pa at temperatures of 1123 to 1773 K [12].

Computational study also reveals that with 67% O-coverage, the diamond (111) surface becomes amorphous but still has sp³ bond character. Oxidized in 95 kPa O₂ at 823 K, the surface of CVD diamond ET100 has approximately 50% coverage[3, 12-14]. The Auger spectrum of the surface indicates that the surface carbon has an sp² bond character, Figure 2.

Diamond (100) and (110) Surfaces
The (100) and (110) surfaces are less reactive as compared to (111) surface. There is no drastic surface reconstruction on these two surfaces. The clean surface and the 100% oxygen coverage remain the retain their sp³ bond character after relaxation. Our simulation clearly shows that O-O single bonds could form on (110) surface.

Figure 3. Relaxation of the clean diamond (111) surface leads to a structure with sp² bond character. The interlayer spacing is 3.40 Å. Note the difference of the structure as compared to Figures 1 and 5.

Figure 4 is placed on the next page due to the large size.

Figure 5. Computer simulation: the sp³ bond character is preserved if the surface is covered by chemisorbed oxygen. Note the analogous as compared to Figure 1.
Figure 6. Phase transition occurs on the diamond (111) surface with 22% chemisorbed oxygen. The surface carbon has an sp² bond character.

Conclusions

Taking both oxidation and phase transition into consideration, we propose that diamond can take either one of two different paths during the heat treatment of diamond in oxygen at elevated temperatures: 1) direct gasification of sp³-bonded carbon; and 2) sp³ to sp² phase transition (surface reconstruction) first, then followed by gasification of sp²-bonded carbon. Diamond oxidation and phase transition are the results of these two competing mechanisms. We further suggest that surface oxygen coverage and temperature are the two most influential factors that govern the surface reaction of diamond. The reaction between oxygen and diamond (111) surface at room pressure is summarized as:

- Elevated temperature (~ 973 K to 1773 K), zero coverage:
  The bond character of diamond (111) surface changes from sp³ to sp². Thus, diamond goes through a phase transition and forms amorphous, sp²-bonded carbon.

- Elevated temperature (~ 973 K and higher), low coverage (up to 20%):
  Diamond converts to amorphous, sp²-bonded carbon first. Then the oxidation of carbon proceeds, yielding gaseous products CO and/or CO₂.

- Elevated temperature (~ 773 K and higher), high coverage (more than 50%):
  Diamond converts to amorphous, sp³-bonded carbon first. Then the oxidation proceeds, yielding gaseous products CO and/or CO₂.

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References

Figure 4. TEM image and electron diffraction pattern of the carbon layer formed during the treatment of CVD diamond ET 100 at 1741 °C in 6x10⁻¹⁰ Pa O₂ for 600 min. The blur diffraction rings at the corner suggest the amorphous nature of the carbon layer.