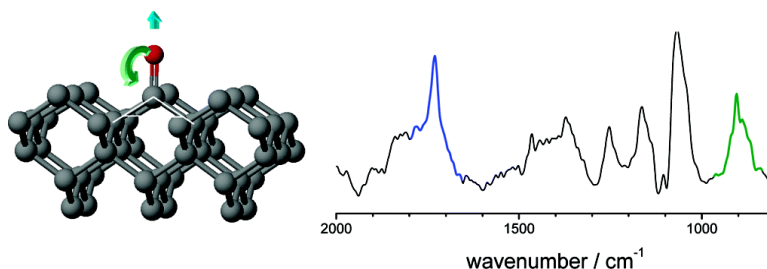Communication

The Oxidation of Diamond: The Geometry and Stretching Frequency of Carbonyl on the (100) Surface

Phillip John, Neil Polwart, Clare E. Troupe, and John I. B. Wilson

More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 1 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

The Oxidation of Diamond: The Geometry and Stretching Frequency of Carbonyl on the (100) Surface

Phillip John,* Neil Polwart, Clare E. Troupe, and John I. B. Wilson

School of Engineering and Physical Sciences, Heriot-Watt University, Riccarton, Edinburgh EH14 4AS, U.K.

Received December 4, 2002; E-mail: P.John@hw.ac.uk

Oxygen on diamond surfaces influence important properties such as chemical reactivity,[1,2] field emission,[3,4] electrical conductivity,[5,6] and Schottky barrier heights.[7] It has become appreciated[7] that the electronic properties depend on the geometry and configuration of the oxygen group on the surface. Techniques for oxygenating diamond include thermal,[8-11] plasma,[12] and electrochemical techniques.[13] The thermal oxidation of natural diamond has been studied extensively.[9-11,14] With the advent of crystallographically improved CVD diamond, we elucidate the detailed mechanism of thermal oxidation by probing the residual surface oxygen groups.

Creating atomically smooth surfaces of low index planes of natural diamond by mechanical polishing is a difficult, if not an intractable, problem.[15] Microscopic ridges are formed, destroying the atomic regularity. Similarly, fracture surfaces of diamond predominantly reveal[16] (111) planes. Moreover, the oxidation of both synthetic HPHT and natural (100) diamond results in the well-documented[14] formation of microfacets, bound by (111) surfaces. To date, the presence of isolated carbonyl groups on atomically regular diamond (100) surfaces has not been unequivocally demonstrated. We have previously studied[8] the kinetics and mechanism of CVD diamond oxidation using a combination of laser interferometery, thermogravimetric analysis, and atomic force microscopy. High-quality (100) facetted microwave plasma enhanced chemical vapor deposition (MPECVD) films oxidize via layer-by-layer removal with none of the macroscopic etch defects associated with natural diamond.

In this paper, we present diffuse reflectance infrared Fourier transform (DRIFT) spectra of oxidized (100) diamond crystallites produced by MPECVD.

Facetted (100) polycrystalline diamond films were grown on (100) single-crystal silicon by microwave (2.45 GHz) plasma deposition. Localized epitaxial diamond growth has previously been fully documented, and the plasma parameters adopted for each step have been given elsewhere.[17] Five distinct sequential plasma treatments were employed: (i) an initial hydrogen etch, (ii) carburization in a H_2/CH_4 mixture, (iii) bias nucleation at −320 V, (iv) growth in a $H_2/CH_4/CO$ mixture, and (v) a final hydrogen plasma etch. The surface temperatures of the diamond films during growth were measured by two wavelength pyrometry at $\lambda = 1.19$ and 1.25 μm. The duration of the final stage determines the ultimate roughness of the surface.[18] Treatment times in excess of 10 h are required to yield atomically smooth crystallites.[18] Films were thermally oxidized at temperatures above 500 °C, in 11−760 Torr of dry oxygen (<8 vpm H_2O, measured with a MEECO model Z H_2O analyzer), for times up to 4 h (i.e., up to 10^{13} langmuir). The chamber was evacuated to better than 10^{-6} Torr prior to oxidation. Following oxidation, the films were cooled rapidly, and the infrared spectrum was recorded, in a Biorad FTS60 FTIR spectrometer equipped with an MCT detector and diffuse reflectance accessory referenced to a clean mirror polished (100) silicon wafer. For comparison, the DRIFT spectrum of 2-adamantanone (>99%,

Aldrich) was measured with respect to a gold reference material. 2-Adamantanone was selected due to its stark structural similarity to the repeating unit predicted for the carbonyl-terminated surface of diamond.[19] The films were subject to X-ray photoelectron spectroscopy (XPS) analysis using Al Kα radiation in an ESCA 300 instrument.[20]

XPS of the near surface region of the films revealed only the presence of carbon (C1s, BE = 284.5 eV) and oxygen (O1s, BE = 532 eV). Deconvolution of the C1s envelope reveals six distinct components, including two peaks shifted to +1.16 and +1.87 eV from the main diamond peak assigned[8] as ether (C−O−C) and carbonyl (C=O) moieties, respectively. In vacuo heating of the sample (up to 750 °C), combined with angle resolved (20−90°) XPS, demonstrates that this oxygen is chemisorbed at the extreme outer surface of the crystallites.[8] The surface coverage was ascertained to be approximately one monolayer on the basis of the analysis of the calibrated C1s and O1s peak areas.[22]

The kinetics of high-quality (100) CVD diamond oxidation have been studied[8] using thermogravimetric analysis and laser interferometry ($\lambda = 636$ nm). The oxidation rate is $= k P_{O_2}$, and A and Ea are 2.0×10^7 nm s^{-1} Pa^{-1} and 222 kJ mol^{-1}, respectively, where the rate constant obeys the Arrhenius equation. The oxidized films retain the (100) facets, and the roughness of the surface remains constant, as evidenced by atomic force microscopy of single crystallites after the removal of up to 6×10^3 atomic layers. Figure 1 shows the DRIFT spectrum of the oxidized diamond surface in the range 2000−800 cm^{-1}. A distinct band at 1731 cm^{-1} was observed. This band is assigned to the stretching mode, $\nu_s(C=O)$, of a carbonyl group, on the basis of its proximity to the equivalent mode in 2-adamantanone (1732 cm^{-1})[21] and the known frequencies of alternative oxygen-containing functional groups.[23,24] In all of the samples with the latter, a second feature was also observed at 905 cm^{-1}. The peak at 1068 cm^{-1} is assigned[25] to the Si−O−Si asymmetric stretch in the underlying substrate. Peaks are clearly observed at 1464, 1373, 1253, 1165, and 1104 cm^{-1}. A large, broad peak at 2870 cm^{-1} was also observed and assigned[26] to the CH$_x$ stretching modes of intergranular hydrogen. The complexity and the close proximity of the peaks in the 1500−1000 cm^{-1} region make it difficult to accurately assign these features. Studies on diamond normally assign these features to C−H bending or C−C and C−O stretches. However, there remains uncertainty[9,19,27] over the exact assignment.

No peak was observed at 1332 cm^{-1}, which arises when a defect-induced loss of symmetry results in the lattice vibration becoming IR active.[9]

Pioneering work[23] on the oxidation of diamond dust identified a plethora of oxygenated groups, dominated by ether (C−O−C), carbonyl (>C=O), hydroxyl (−OH), carboxylic acid (−COOH), and anhydride (−CO−O−CO−) groups. However, the poorly defined surfaces of diamond dusts make it impossible to interpret the geometry of those groups.
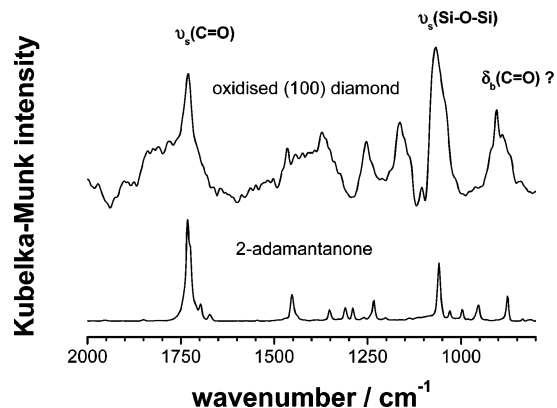
Figure 1. DRIFT spectra of (100) diamond oxidized at 700 °C, for 10 min in 150 Torr O_2, and powdered 2-adamantanone − the vibrational spectrum of 2-adamantanone has been assigned[21] previously.
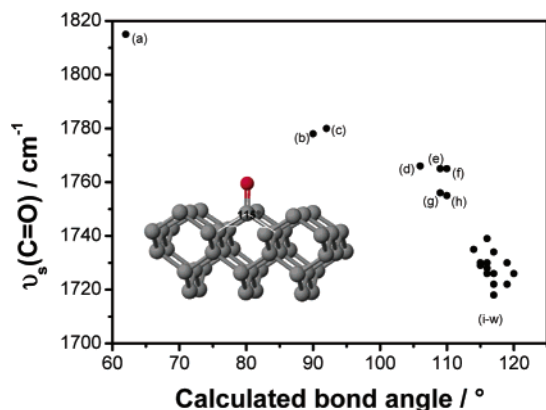

Figure 2. Correlation between bond angle and gas-phase CO stretching frequency for a range of ketone structures: (a) cyclopropanone, (b) spiro bicyclo[3.2.0]heptane-6,1′-cyclohexanone, (c) cyclobutanone, (d) bicyclo-[2.2.1]-2-heptanone, (e) 3,4-dimethyl cyclopentanone, (f) cyclopentanone, (g) 2,2-dimethylcyclopentanone, (h) 2-cyclopentyl cyclopentanone, (i) cyclohexane, (j) 2-decanone, (k) 3-hexanone, (l) 3-octanone, (m) 2-methyl-5-nonanone, (n) 5-decanone, (o) 3-dodecanone, (p) acetone, (q) cyclooctanone, (r) 2-octanone, (s) 2-methyl-3-nonanone, (t) 2-methyl-3-nonanone, (u) cycloheptanone, (v) 4-decanone, (w) 3-decanone. The dihedral angle of 2-adamantanone is calculated to be 115°. The inset shows the carbonyl group on (100) diamond.

Recently, the vibrational spectroscopy of oxidized single-crystal diamond has been studied[9−11] using electron energy loss spectroscopy (EELS). Features at 1720−1820 cm^{-1} were attributed to functional groups containing carbonyl; however, the movement of peaks to higher wavenumber with increasing oxygen coverage suggests the formation of higher oxidation states (e.g., lactones, anhydrides, etc.) at step edges. Hossain et al. performed similar investigations[19] on boron doped homoepitaxial samples using EELS. The ν_s(C=O) and δ_b(C=O) were assigned to bands at ~1734 and 911 cm^{-1}, respectively. Unfortunately, the roughness of the samples is not discussed. The spectral resolution of FTIR spectroscopy is greater that that of EELS, allowing a more accurate interpretation of the geometry based on our results.

Calculation of ν_s(C=O) is not trivial. The best theoretical calculations reported[19] to date show significant error both for diamond surfaces (1777 cm^{-1}) and for the 2-adamantanone analogue (1789 cm^{-1}), although large differences between the calculation and experimental results are not uncommon.

The frequency of ν_s(C=O) varies with the geometry of the carbonyl group.[28] The ν_s(C=O) frequency of various ketone compounds was obtained from the NIST database.[29] PM3 molecular dynamics in the CAChe software[30] were employed to determine

the structure of these compounds. Evidently, from Figure 2, the dihedral angle of the carbonyl group on the diamond surface is close to that of 2-adamantanone and other nonstrained six-membered ring structures.

The relative stability of different oxygen-containing functional groups on (100) diamond surfaces has been the subject of some debate.[11,19,23,27,31−33] This is the first direct evidence of the presence of carbonyl groups as part of unstrained six-membered rings, on (100) diamond surfaces. Such structures are important intermediates in the predicted[33] mechanism for diamond oxidation. The latter model predicts that the chemisorption of O_2 onto a (100) diamond surface has the highest activation barrier within the reaction scheme. These results provide new evidence in support of this mechanism of diamond oxidation.

References

(1) Foord, J. S.; Hian, L. C.; Jackman, R. B. *Diamond Relat. Mater.* **2001**, *10*, 710.
(2) Notsu, H.; Yagi, I.; Tatsuma, T.; Tryk, D. A.; Fujishima, A. *J. Electroanal. Chem.* **2000**, *492*, 31.
(3) Wilson, J. I. B.; Walton, J. S.; Beamson, G. *J. Electron Spectrosc. Relat. Phenom.* **2001**, *121*, 183.
(4) Yamada, T.; Yokoyama, T.; Sawabe, A. *Diamond Relat. Mater.* **2002**, *11*, 780.
(5) Shirafuji, J.; Sugino, T. *Diamond Relat. Mater.* **1996**, *5*, 706.
(6) Foord, J. S.; Lau, C. H.; Hiramatsu, M.; Jackman, R. B.; Nebel, C. E.; Bergonzo, P. *Diamond Relat. Mater.* **2002**, *11*, 856.
(7) Saby, C.; Muret, P. *Diamond Relat. Mater.* **2002**, *11*, 851.
(8) John, P.; Polwart, N.; Troupe, C. E.; Wilson, J. I. B. *Diamond Relat. Mater.* **2002**, *11*, 861.
(9) Pehrsson, P. E.; Mercer, T. W.; Chaney, J. A. *Surf. Sci.* **2002**, *497*, 13.
(10) Pehrsson, P. E.; Mercer, T. W. *Surf. Sci.* **2000**, *460*, 49.
(11) Pehrsson, P. E.; Mercer, T. W. *Surf. Sci.* **2000**, *460*, 74.
(12) Notsu, H.; Yagi, I.; Tatsuma, T.; Tryk, D. A.; Fujishima, A. *Electrochem. Solid-State Lett.* **1999**, *2*, 522.
(13) Goeting; Gutierrez-Sosa; Foord. *Electrochemically Induced Surface Modifications of Boron-Doped Diamond Electrodes: An X-ray Photoelectron Spectroscopy Study*; CLRC: Daresbury, U.K., 1998.
(14) de Theije, F. K.; van der Laag, N. J.; Plomp, M.; Van Enckevort, W. *Philos. Mag. A* **2000**, *80*, 725.
(15) Couto, M. S.; Vanenckevort, W.; Seal, M. *Philos. Mag. B* **1994**, *69*, 621.
(16) Telling, R. H.; Pickard, C. J.; Payne, M. C.; Field, J. E. *Phys. Rev. Lett.* **2000**, *84*, 5160.
(17) John, P.; Milne, D. K.; Roberts, P. G.; Jubber, M. G.; Liehr, M.; Wilson, J. I. B. *J. Mater. Res.* **1994**, *9*, 3083.
(18) Fitzgerald, A. G.; Fan, Y.; John, P.; Troupe, C. E.; Wilson, J. *J. Vac. Sci. Technol., B* **2000**, *18*, 2714.
(19) Hossain, M. Z.; Kubo, T.; Aruga, T.; Takagi, N.; Tsuno, T.; Fujimori, N.; Nishijima, M. *Surf. Sci.* **1999**, *436*, 63.
(20) Beamson, G.; Briggs, D.; Davies, S. F.; Fletcher, I. W.; Clark, D. T.; Howard, J.; Gelius, U.; Wannberg, B.; Balzer, P. *Surf. Interface Anal.* **1990**, *15*, 541.
(21) Bistricic, L.; Baranovic, G.; Mlinaric-majerski, K. *Spectrochim. Acta, Part A* **1998**, *54*, 1961.
(22) Seah, M. P. In *Auger and X-ray Photoelectron Spectroscopy*, 2nd ed.; Briggs, D., Seah, M. P., Eds.; John Wiley & Sons: England, 1990; Vol. 1.
(23) Ando, T.; Yamamoto, K.; Ishii, M.; Kamo, M.; Sato, Y. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 3635.
(24) Martin, H. B.; Morrison, P. W. *Electrochem. Solid-State Lett.* **2001**, *4*, 17.
(25) Queeney, K. T.; Weldon, M. K.; Chang, J. P.; Chabal, Y. J.; Gurevich, A. B.; Sapjeta, J.; Opila, R. L. *J. Appl. Phys.* **2000**, *87*, 1322.
(26) John, P.; Milne, D. K.; Drummond, I. C.; Jubber, M. G.; Wilson, J. I. B.; Savage, J. A. *Diamond Relat. Mater.* **1994**, *3*, 486.
(27) Struck, L. M.; Develyn, M. P. *J. Vac. Sci. Technol., A* **1993**, *11*, 1992.
(28) Kemp, W. *Organic Spectroscopy*, 3rd ed.; MacMillan Press Ltd: Hampshire, U.K., 1991.
(29) Linstrom, P.; Mallard, W. *NIST Chemistry Webbook*; National Institute of Standards and Technology: Gaithersburg MD, 2001 (http://webbook.nist.gov/chemistry/).
(30) Check, C. E.; Gilbert, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 9566.
(31) Skokov, S.; Weiner, B.; Frenklach, M. *Phys. Rev. B* **1997**, *55*, 1895.
(32) Zheng, J. C.; Xie, X. N.; Wee, A. T.; Loh, K. P. *Diamond Relat. Mater.* **2001**, *10*, 500.
(33) Skokov, S.; Weiner, B.; Frenklach, M. *Phys. Rev. B* **1994**, *49*, 11374.

JA029586A