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Grant N00014-91-J-1550

R&T Code: 413w003

Technical Report No. 19

Infrared spectroscopy of hydrogen and water on diamond (100)

by

L. M. Struck and M. P. D'Evelyn

Prepared for publication in

Diamond Materials (Proc. 3rd International Symposium)

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May 29, 1993

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No 0704-0188*

1. AGENCY USE ONLY (*Leave blank*)	2. REPORT DATE May 1993	3. REPORT TYPE AND DATES COVERED Technical

4. TITLE AND SUBTITLE

Infrared spectroscopy of hydrogen and water
on diamond (100)

5. FUNDING NUMBERS

Grant #:
N00014-91-J-1550

6. AUTHOR(S)

L. M. Struck and M. P. D'Evelyn

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Rice University
Department of Chemistry
Houston, TX 77251-1892

8. PERFORMING ORGANIZATION REPORT NUMBER

Technical Report
#19

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Prepared for publication in:
Diamond Materials (Proc. 3rd International Symposium)

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

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14. SUBJECT TERMS

Diamond, hydrogen, water, infrared spectroscopy,
chemical vapor deposition

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT

NSN 7540-01-280-5500

Standard Form 298 (Rev 2-89)
Prescribed by ANSI Std Z39-18
298-102

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INFRARED SPECTROSCOPY OF HYDROGEN AND WATER ON DIAMOND (100)

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ABSTRACT

The adsorption of deuterium and water on diamond (100) has been investigated by infrared multiple-internal-reflection spectroscopy using a natural type IIa diamond internal reflection element. Evidence was seen for both monohydride surface species (CD deformation mode at 901 cm^{-1}) and dihydride species (CD_2 deformation mode at 1125 cm^{-1}). Following exposure to water at elevated temperature, infrared modes were detected at 1280, 1200, 1125, 1080, and 720 cm^{-1}, and are assigned to ether (C–O–C), hydroxyl (C–OH), and carbonyl (>C=O) modes. The substantial observed reactivity of diamond with water indicates a potentially important role for surface hydroxyl and oxide species in diamond growth.

INTRODUCTION

There is much interest in understanding diamond chemical vapor deposition (CVD) at a fundamental level, and the greatest uncertainties in the growth mechanism(s) at present unquestionably pertain to the surface chemistry. Studies on single crystal surfaces of diamond allow the relationship between surface structure and chemical reactivity to be explored systematically. The (100) surface of diamond is likely to be the most important of the low-Miller-index faces, as it is prevalent in growth (1) and is typically the only low-index orientation where the actual surface of CVD films resembles the nominal orientation (i.e., the surface is smooth on the nanometer-to-micron scale) (2-4). It is also the crystal face most likely to be useful for atomic layer epitaxy (5).

The critical role played by hydrogen in diamond chemical vapor deposition (CVD) is well established (1). Several groups have investigated the interaction of hydrogen with diamond (100) (6-8), but important questions remain. In particular, the kinetics of formation, relative stabilities (6-9), and preponderance during growth (3,10) of monohydride (CH) and dihydride (CH_2) species, with one or two hydrogen atoms bonded to surface carbon atoms, respectively, is in dispute.

The addition of oxygen to diamond growth environments can greatly enhance diamond film quality, particularly at high hydrocarbon concentrations or at low substrate temperatures (11-14). There is also considerable interest in growth from oxy-acetylene torches (15) and using oxygen-containing precursors (16). Mechanistic studies of the effects of oxygen addition have focused mainly on the gas phase chemistry and the possible modification of the surface chemistry by OH radicals (17-19). However, *water* is produced in diamond growth reactors (20,21) upon addition of O_2 or oxygen-containing

Proc. 3rd Int. Symp. Diamond Materials (The Electrochemical Society, 1993)

precursors and is present at impurity levels in all reactors, yet water-diamond reactions are neglected in all existing diamond growth models. In addition, although several groups have studied the adsorption of water on diamond powder (22-24) and Thomas *et al.* recently investigated the interaction of oxygen atoms with diamond (100) (25), single-crystal surface studies of the interaction of H_2O with diamond have not yet been reported.

EXPERIMENTAL METHOD

We have investigated the interaction of deuterium and water with diamond (100) by infrared multiple-internal-reflection spectroscopy (IMIRS) in an apparatus described previously (8). Briefly, collimated light from a Fourier-transform infrared spectrometer is focused through a differentially-pumped KBr window onto one beveled edge of a diamond internal reflection element (IRE) inside an ultrahigh vacuum chamber. The diamond sample is shown schematically in Fig. 1. After undergoing approximately 33 internal reflections from each face to enhance sensitivity to surface species, the infrared light is transmitted through the opposite beveled edge of the diamond IRE and is collected and focused onto a detector. Diamond is effectively opaque at this long path length for frequencies between 1600 and 2800 cm^{-1}, preventing the observation of C=O stretching modes, and the transmitted intensity at frequencies below 1500 cm^{-1} is considerably greater than that above 2800 cm^{-1}, so that sensitivity is greatest in the "fingerprint" region of the spectrum.

Following degreasing, the diamond sample was cleaned by simply heating in ultrahigh vacuum (6,7,25-27). In the hydrogen/deuterium experiments the sample was heated to only ≈ 550 K (the temperature could not be accurately measured), and therefore the surface was probably partially contaminated by oxygen. In the water experiments the sample was heated as high as 1270 K.

Exposures of the diamond (100) IRE to atomic hydrogen or deuterium were made by backfilling the reactor cell with H_2 or D_2, respectively, at pressures between 1×10^{-8} and 1×10^{-7} Torr for up to one hour. The W filament was located approximately 1 cm above the sample and was heated to 1700-1800 K. Water exposures were made by backfilling the reactor cell while the diamond sample was heated and subsequently cooled. Reactions with hydrogen atoms presumably took place on the top surface only, while adsorption and reaction of water likely took place on both the top and bottom faces.

RESULTS

Infrared spectra taken following 50 L and 90 L nominal exposures (1 L = 10^{-6} Torr sec) of the hydrogenated diamond (100) sample to atomic deuterium are shown in Fig. 2. The absorption feature at 901 cm^{-1} in Fig. 2(a) is assigned to a C-D deformation mode of monohydride surface species, with one hydrogen atom per surface carbon atom. The 1125 cm^{-1} feature in Fig. 2(b) is assigned to a CD_2 deformation mode of dihydride surface species. We believe that CD monohydride species were also present on the surface when the latter spectrum was acquired, but ice formation in the infrared detector prevented observation of modes below 1000 cm^{-1} in this particular experiment. Both spectral assignments are based on a comparison of the surface mode frequencies with those of perdeuterated adamantane, $C_{10}D_{16}$, which has CD deformation modes at 901 and 996 cm^{-1} and CD_2

deformation modes at 1071, 1110, and 1215 cm^{-1} which are split by the tetrahedral symmetry of the molecule (28). Trace amounts of hydrocarbon impurities in the infrared detector lead to spurious CH_x peaks which are difficult to distinguish from absorption features due to surface CH_x species. We are therefore unable to confidently assign infrared peaks associated with surface hydrogen and report only the surface deuteride results. For brevity we use the terms hydride and deuteride interchangeably in describing surface species. Details of the spectral assignments are described elsewhere (29).

Exposure of the deuterated diamond (100) surface to atomic hydrogen, also at about 500 K, caused the disappearance of both the 901 and 1125 cm^{-1} CD and CD_2 modes, consistent with the spectral assignments and with the presumed ability of gas phase atomic hydrogen to abstract surface hydrogen.

The IMIRS spectrum shown in Fig. 3(a) was obtained by heating the diamond sample to 1070 K for ten minutes and then cooling it in a pressure of 1×10^{-7} Torr of water. Similar results were obtained in experiments where the maximum annealing temperature was 1400 K. In a second set of experiments, the diamond sample, which had been previously oxidized, was heated to ≈1270 K while maintaining the chamber pressure below 4×10^{-9} torr. The peaks seen in Fig. 3(b) correspond to surface species that desorbed or reacted to form different species upon heating. The infrared spectra indicate the formation of several surface oxides, with strong peaks at 1250, 1200, 1125, 1080, and 720 cm^{-1}. The multiple-peak features of the 1250-1200 cm^{-1} band and the 1080 cm^{-1} band were found to be quite reproducible. Since products of oxygen adsorption (CO, CO_2) desorb near 870 K (23,25), water adsorption most likely occurred as the sample temperature dropped below the desorption threshold.

Assignments of the infrared peaks shown in Fig. 4 were made primarily by comparison to spectra of substituted adamantanes. The 1125 and 1080 cm^{-1} features are assigned to vibrational modes of surface hydroxyl (-OH) species, based on the similarity in their frequences to analogous modes in 1-adamantanol at 1115 and 1087 cm^{-1} (30). The 1250 and 1200 cm^{-1} bands, which we assign to C-O stretching modes in an ether-type or bridge-bonded oxygen (C-O-C) structure, did not always appear upon gas exposures or disappear upon annealing concurrently with the 1125 and 1080 cm^{-1} bands, implying that the former are associated with a surface species other than OH. We have not yet been able to obtain infrared or Raman spectra of 2-oxa-adamantane, and the assignment of the 1250 and 1200 cm^{-1} bands to bridge-bonded oxygen is based on a comparison with experimental data on other cyclic ethers (31,32) and to predicted frequencies for 2-oxa-adamantane obtained from *ab initio* self-consistent-field (SCF) calculations that we performed using Gaussian 92 (33). Finally, the 720 cm^{-1} feature is tentatively assigned to a carbonyl (>C=O) bending mode based on the corresponding mode in 2-adamantone (860 cm^{-1}) (34).

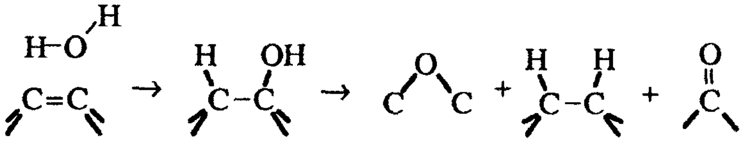
DISCUSSION

The present results represent the first observation of the C-D bending modes for monohydride and dihydride species on diamond (100). We argue that the apparent facile formation of dihydride species on diamond (100) contradicts neither the observation by

Thomas *et al.* (7) that atomic hydrogen does not readily break the C-C dimer bond present in the 2×1 reconstruction nor the extreme steric repulsion predicted for the 1×1 dihydride by Yang and D'Evelyn (9). Couto *et al.* showed by scanning tunneling microscopy that an as-polished diamond (100) surface was covered with grooves and ridges 10-30 nm in height with local slopes as high as 30°, implying a high concentration of atomic steps (35). We made qualitatively similar observations by atomic force microscopy (3). Dihydride formation on step edges would not require dimer-bond breaking and also would not generate significant steric repulsion as would neighboring CH_2 species on flat (100) terraces. Further work is needed to address the relative thermal stabilities of monohydride and dihydride species, the effects of coadsorbed oxygen, and the relationship between the nanometer-scale morphology and the propensity for dihydride formation.

Our observations of the infrared modes of hydroxyl and oxide species, a first on diamond (100), are consistent with previous experiments on diamond powder. Infrared features near 1270 cm^{-1} observed following exposure of diamond powder to oxygen were assigned to bridge-bonded surface oxygen (22,23). Modes near 1780 cm^{-1} were also observed on diamond powder and assigned to surface carbonyl species (22,23). The spectral range between 1600 and 2700 cm^{-1} is inaccessible in IMIRS due to absorption by the bulk lattice, but the 720 cm^{-1} mode we observed in some of the experiments is consistent with surface carbonyl formation. Modes assigned to hydroxyl species on diamond powder have not yet been reported, but a broad infrared feature near 1100 cm^{-1}, assigned to an ether species (22), may in fact have been due to hydroxyl instead.

We postulate that the observed surface oxide species were formed by dissociative adsorption of water followed by further decomposition. Based on an analogy between dissociative adsorption and molecular addition reactions (36), the reaction of water with diamond (100) may occur on a single dimer, as indicated in Eq. (1),



(1)

forming H(a) + OH(a), as occurs on Si(100) (37) and on Ge(100) (38). We propose that decomposition took place concurrently with adsorption since the water exposures in our experiments were made at elevated temperatures, resulting in a mixed adlayer of hydroxyl, bridge-bonded oxygen, carbonyl, and hydride species. We obtained the infrared spectra of oxide species (Fig. 3) using a detector that has a wider spectral range but a lower sensitivity than the detector used to observe D(a) (Fig. 2), and therefore coadsorbed hydride species could not be observed.

Perhaps the most significant result reported here from the standpoint of diamond CVD is that water reacts readily with diamond. We estimate a reactive sticking coefficient of 10^{-3}-10^{-2}. Water is present at impurity levels in essentially all CVD reactors and at substantial concentrations when oxygenated precursors are employed or O_2 is added. Although the sticking coefficient for OH radicals is certainly much higher than that of water, the flux onto the surface should be much lower. In simulations of diamond growth from an oxy-acetylene flame, Meeks and coworkers calculated an OH radical flux that was lower by nearly four orders of magnitude than that of water (39). Therefore, the present results indicate that surface oxide formation may be important in diamond CVD and that water adsorption is likely to be the dominant channel for the formation of surface oxides. Diamond CVD is typically carried out at substrate temperatures above 600 °C, where thermal desorption of surface oxides occurs at substantial rates (23,25), producing predominantly CO at low surface oxygen coverages (25). Therefore, each H_2O molecule adsorbed during growth most likely produces adsorption of two hydrogen atoms and etching of one surface (sp^3) carbon atom, modifying the atomic-scale morphology and perhaps also leading to preferential etching of graphite. Given the reactivity of diamond with water and the prevalence of water in diamond CVD environments, we suggest that the adsorption and decomposition of water may play an important role in diamond CVD.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the National Science Foundation (Grants CHE-8807546 and CHE-9214328) and the Office of Naval Research for support of this work, and thank Dr. K. Raghavachari for assistance with the spectral assignments.

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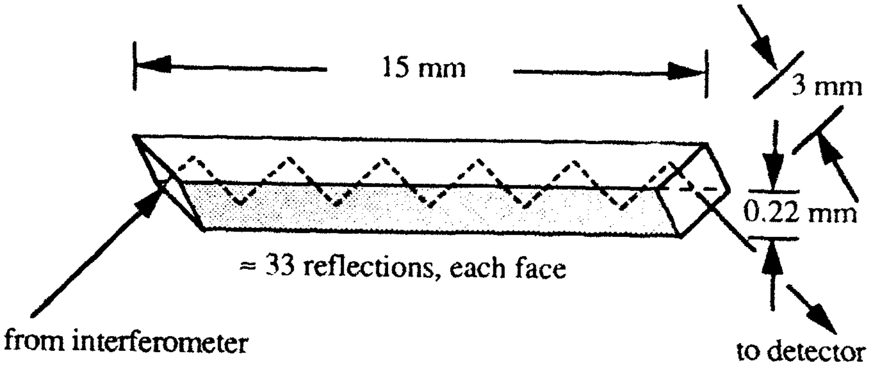

FIG. 1. Schematic view from below of type IIa diamond (100) internal reflection element, $15 \times 3 \times 0.22$ cm^3 in dimension, with a (100) orientation on the large-area faces and ends beveled at 45°.

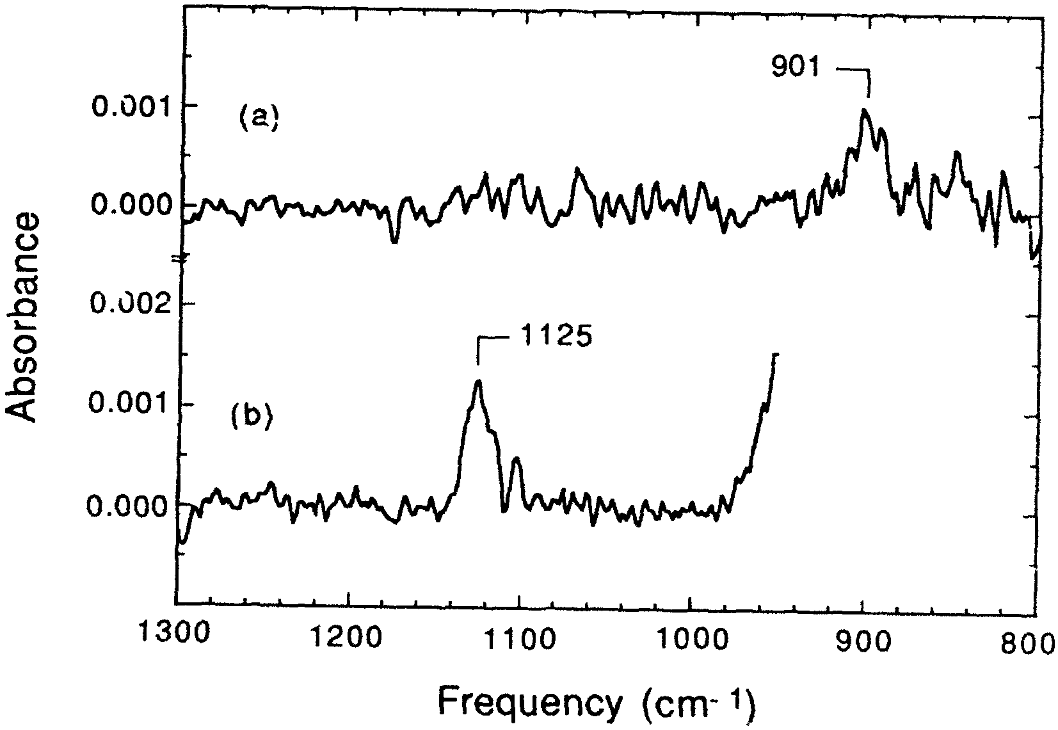

FIG. 2. Infrared multiple-internal reflection spectrum, taken at 4 cm^{-1} resolution with 1024 scans, of CD and CD_2 species on diamond (100). Deuterated surfaces were prepared with (a) 50 L; (b) 90 L nominal doses of a hydrogenated surface at a sample temperature of 500 K.

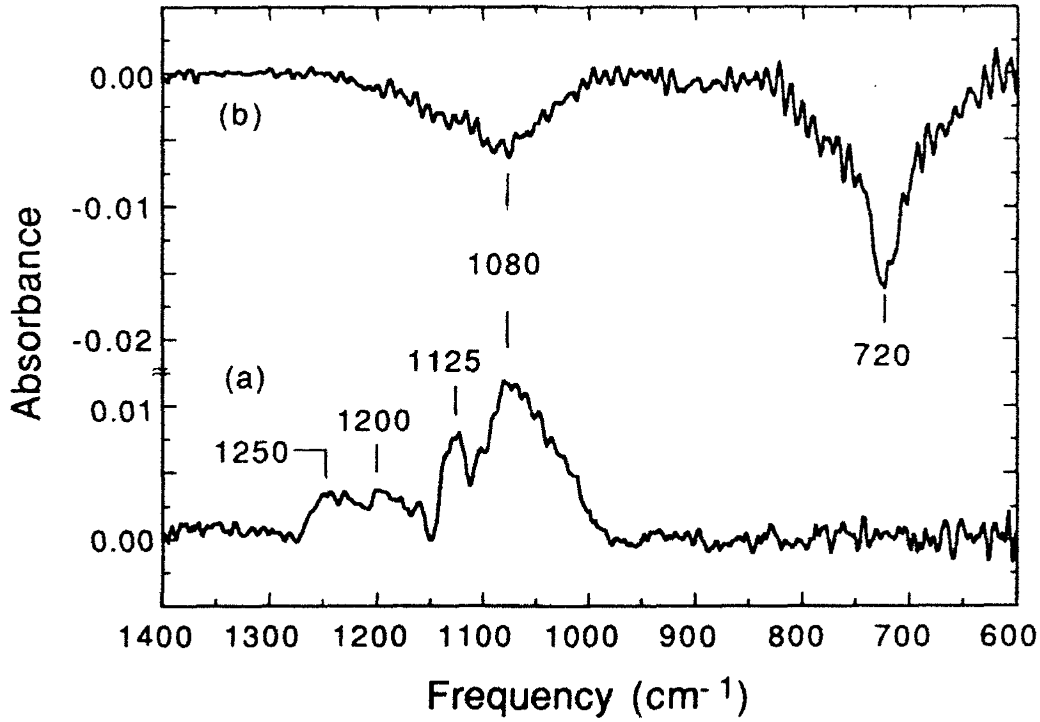

FIG. 3. IMIRS spectra (4 cm^{-1} resolution, 400 scans) obtained by (a) cooling the sample from ≈1070 K in 1×10^{-7} Torr of H_2O; or (b) heating an oxidized surface to ≈1270 K in UHV. The 1250 and 1200 cm^{-1} features are assigned to bridge-bonded oxygen (C-O-C), the 1125 and 1080 cm^{-1} modes to hydroxyl (-OH), and the 720 cm^{-1} feature to carbonyl (>C=O) species .