

Electrochemically induced surface chemistry and negative electron affinity on diamond (100)

Pehr E. Pehrsson, J. P. Long, Michael J. Marchywka, and James E. Butler
Naval Research Laboratory, Washington, DC 20375

(Received 19 June 1995; accepted for publication 9 October 1995)

Hydrogenated single crystal (100) diamond surfaces subjected to an electrochemical (EC) treatment are selectively oxidized at room temperature. Part of the surface remains hydrogenated, except for a narrow transition region between the oxidized and hydrogenated regions. Ultraviolet photoelectron spectroscopy indicates that the transition region has negative electron affinity (NEA), as do the surfaces of hydrogenated crystals. The oxidized and hydrogenated parts of the EC-treated surfaces do not have NEA. A possible explanation is that contaminants eliminate NEA in the hydrogenated parts of the EC treated surfaces, but the transition region remains uncontaminated. None of the oxidized surfaces exhibit NEA. © 1995 American Institute of Physics.

Surface chemistry and structure can strongly effect electron affinity (χ), defined as the energy difference between the vacuum level and the conduction band minimum (CBM). Negative electron affinity (NEA) is the condition in which the conduction band minimum (CBM) of a material lies higher in energy than the vacuum level, allowing conduction band electrons near the surface to move from the sample into vacuum.¹ Hydrogenated C(111) and C(100) surfaces have a negative χ , but surface modification by heating in vacuum to desorb the hydrogen and reconstruct the surfaces²⁻⁵ or oxidation⁶⁻⁸ makes χ positive, i.e., the vacuum level moves above the CBM. In this work, hydrogenated C(100) surfaces were modified by an electrochemical (EC) technique to further explore surface chemistry effects on χ . The EC treatment oxidizes part of the surface at room temperature while leaving the rest of the surface relatively unchanged, thereby providing distinct surface terminations on one sample.⁹

Natural, semiconducting, type IIB, $4 \times 4 \times 0.25$ mm diamonds polished to $\leq 3^\circ$ of the (100) face¹⁰ were boiled in acids¹¹ to remove metal and nondiamond carbon contaminants, and then hydrogenated and smoothed for 2 h in a 10 Torr, 600 W, hydrogen microwave plasma, at $T_{\text{sub}} = 800^\circ\text{C}$.¹² Some diamonds were then reoxidized either by immersion in boiling acids or by subjecting them to a 200 W microwave oxygen plasma for 8 min at 50 Torr of O_2 , or by dosing with activated molecular oxygen (2×10^{-6} Torr) produced with an iridium filament resistively heated to $1130 \pm 30^\circ\text{C}$.

The EC treatment studied here was previously used to separate homoepitaxial CVD diamond layers from diamond substrates implanted with C^+ ions.¹⁰ In the EC treatment, a diamond is placed between two graphite electrodes immersed in distilled water, with the long crystal dimension parallel to the interelectrode axis. Biases of 30–500 V were applied between the electrodes for times from 2 to 1800 s. The results described below were insensitive to bias voltages and times.

The presence of NEA, as well as differences in electron affinity and band bending, were assessed for the EC-treated samples and for hydrogenated and plasma-oxidized reference surfaces, by ultraviolet photoelectron spectroscopy (UPS) on

beam line X24C of the National Synchrotron Light Source at Brookhaven National Laboratory. The samples were mounted in an unbaked chamber operating at 10^{-9} Torr and equipped with a cylindrical mirror analyzer. A variable slit allowed selective irradiation of the sample surface. Samples were biased at -5 V to facilitate collection of low energy electrons emitted during interrogation with 33 eV photons.

The samples were transported in air to another facility, where XPS was performed using monochromatized $\text{Al } K_\alpha$ radiation (1486 eV) to determine the amount and chemical state of surface oxygen, carbon, and contaminants. Binding energies were referenced to the Fermi level via the $\text{Au } 4f_{7/2}$ peak at 83.93 eV on sputtered Au. The O/C at. % ratios were uncorrected for the fact that the oxygen was restricted to the surface, and therefore should be used only for relative comparison among samples. The diamond surfaces were also characterized at 2×10^{-10} Torr with Auger electron (AES), electron loss (ELS), and secondary electron emission (SEES) spectroscopies and with low energy electron diffraction (LEED). Surface vibrational information was obtained by high resolution electron energy loss spectroscopy (HREELS) using an LK2000 spectrometer.

The plasma-hydrogenated C(100) surfaces displayed sharp, low-background, two-domain 2×1 LEED patterns.¹² The HREELS spectra were dominated by the $2920 \pm 10 \text{ cm}^{-1}$ C–H stretch, assigned to monohydride dimers.¹³⁻¹⁵ *Ex situ* XPS revealed that the O/C ratio was 1 ± 0.3 at. % and that the $\text{C } 1s$ binding energy was 283.8 ± 0.1 eV. Hydrogenated samples exposed to air adsorbed oxygen and/or water over several weeks but the LEED patterns and $\text{C } 1s$ spectra were unchanged. All of the oxidation techniques yielded C(100) surfaces with 1×1 LEED patterns, O/C ratios of 12 ± 2 at. %, and 284.7 ± 0.1 eV $\text{C } 1s$ binding energies. HREELS of the C(100) surfaces oxidized *ex situ* revealed the presence of adsorbed hydrocarbons, which were desorbed by heating to 350°C in UHV. The $\text{C } 1s$ and $\text{O } 1s$ binding energy separation (Δ) was reproducibly 1.2 ± 0.2 eV smaller on the oxidized versus hydrogenated surfaces because of shifts in the $\text{C } 1s$ and $\text{O } 1s$ binding energies. The $\text{O } 1s$ binding energy is consistent with a predominance of carbonyl groups on the

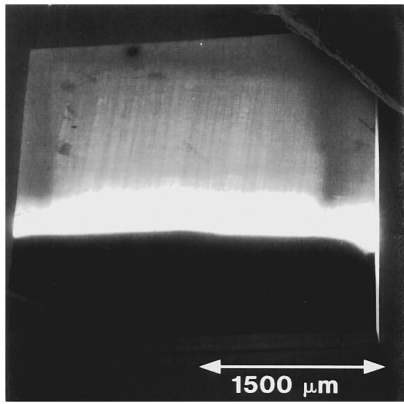


FIG. 1. Scanning electron micrograph of an EC-treated C(100) surface. The top is hydrogenated, the bottom is oxidized, and the bright stripe is the transition region. The upper right- and lower left-hand side corners are obscured by sample clips.

fully oxidized samples, while the C 1s shift probably reflects band bending induced by oxidation.

Hydrogenated C(100) surfaces dosed *in situ* with activated oxygen developed HREELS modes at 1080, 1780, and 3650 cm^{-1} , which we assign to the ether, carbonyl, and hydroxyl stretching frequencies, respectively.^{7,8} The surfaces contained equivalent hydroxyl and carbonyl modes after low doses but only carbonyl groups (and a small, residual C–H stretch mode) at high doses. The vacuum level cutoff on the heavily oxidized surfaces simultaneously increased roughly 3 eV in kinetic energy, probably due to an increased χ . Conductivity measurements with an Ω meter showed that the oxidized surface was far more insulating than the hydrogenated surface, in agreement with other reports.^{16,17} SEM images of hydrogenated (100) surfaces were much brighter than those of oxidized surfaces, consistent with reports that secondary electron emission is much higher on hydrogenated than oxidized C(100) surfaces.¹⁸

The SEM image in Fig. 1 illustrates a corresponding variation in secondary electron emission obtained after EC treatment of a plasma-hydrogenated sample. The dark region at the bottom was nearest the cathode (the induced anode, or IA), and is separated from the brighter, induced cathode (IC) region by a narrow ($<300 \mu\text{m}$), intense stripe. The IC remained largely hydrogenated and exhibited the 2×1 LEED pattern seen on fully hydrogenated surfaces. Its O/C ratio was 2–4 at. %, only slightly above the 1% observed prior to EC treatment. The IA region, on the other hand, was heavily oxidized. The XPS O/C ratio increased to 12–14 at. %, similar to the level generated by the oxidation techniques described above, and the IA wet much more readily with water than the IC, consistent with the presence of polar surface oxygen groups. A 1×1 LEED pattern was observed, as is also seen on fully oxidized samples.

The existence of both oxidized and hydrogenated regions was confirmed by the XPS results of Fig. 2. The C 1s binding energy with respect to the Fermi level on the IA (IC) side was nearly equal that of an oxidized (hydrogenated) reference sample. Most of the apparent 1 eV shift between IA and IC was caused by changes in band bending and not

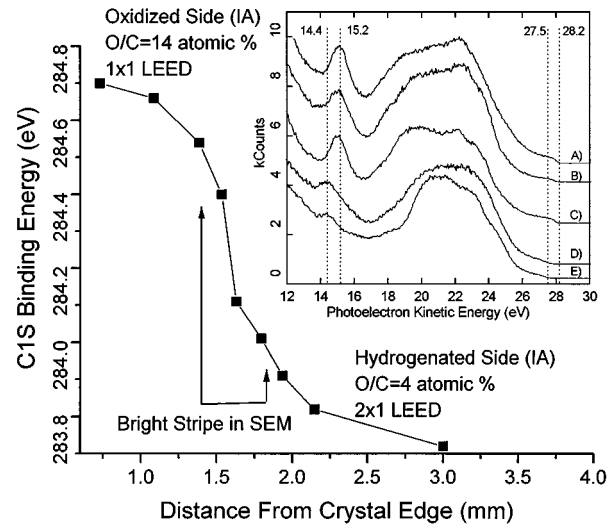


FIG. 2. XPS-C 1s binding energy and C/O at. % ratio of EC-treated C(100). The average C 1s binding energies for oxidized and hydrogenated diamond surfaces are 284.7 and 283.8 eV, respectively. The inset shows UPS (photon energy=33 eV) of the valence band maximum of C(100) surfaces: (a) plasma hydrogenated; (b) transition zone (stripe); (c) hydrogenated side of EC-treated (IC); (d) oxidized side of EC-treated (IA); (e) plasma oxidized.

chemical shifts, as revealed by the 0.8 eV downward shift of the UPS bulk valence band (VB) feature near 14 eV (see inset) as one progressed onto the oxidized region. From the inset, it is also clear that the band bendings of the IA and IC regions equal those of their respective analogs (± 0.1 eV), in spite of a low level of contamination on the EC samples described below.

The techniques discussed so far, including the VB spectra in the inset to Fig. 2, show that the hydrogenated and oxidized reference samples resemble IC and IA regions, respectively, of EC-treated crystals. To specifically address NEA, the secondary electron cutoff in UPS spectra were also compared. The results are presented in Fig. 3, where the cutoffs (dotted lines) were determined by extrapolating the

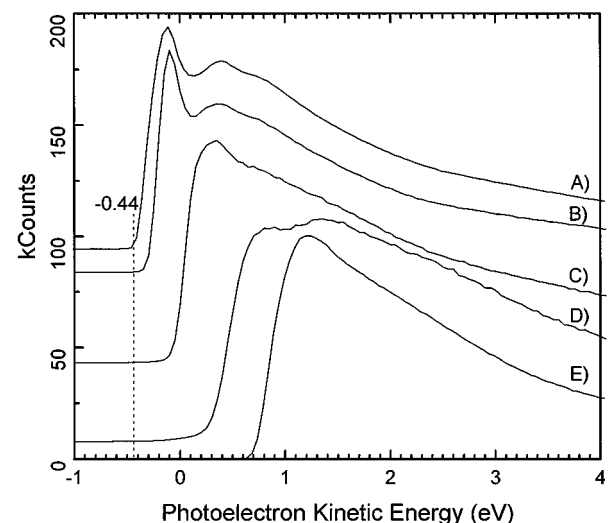


FIG. 3. UPS (photon energy=33 eV) of C(100) surfaces: (a) plasma hydrogenated, (b) transition zone (stripe), (c) hydrogenated side of EC-treated (IC), (d) oxidized side of EC-treated (IA), (e) plasma oxidized. The dotted line is the secondary cutoff discussed.

steepest part of the spectrum to zero intensity. For a surface with positive χ , the cutoff locates the vacuum level; for negative χ , i.e., NEA, it locates the CBM. Viewed in this way, the IA and IC differ from the reference samples: the IA cutoff (curve D) falls 0.4 eV below its oxidized analog (E) while the IC cutoff (C) is 0.3 eV above its plasma-hydrogenated analog (A), an amount sufficient to remove the sharp NEA feature. This feature has been observed by others on hydrogenated surfaces and attributed to NEA, specifically emission of thermalized electrons from the CBM. As is evident in Fig. 3 (curve B), NEA was retained in the transition zone (bright stripe in Fig. 1) of the EC-treated sample.

Secondary electron emission spectroscopy (SEES) and UPS gave similar results on similarly prepared diamond surfaces; only the stripe exhibited an NEA-induced peak on the EC-treated diamonds. NEA was routinely obtained on the hydrogenated C(100) surfaces, but was eliminated by oxidation. The presence of an air- and water-stable NEA zone after the EC treatment might result from a surface dipole layer created by appropriately oriented surface groups, e.g., $-\text{OH}$, with the electronegative oxygen next to the diamond surface and the electropositive hydrogen outermost. Such an atomic arrangement could create a field which accelerated surface electrons into the vacuum, as has previously been observed for CsO on GaAs surfaces.¹ Carbonyl and ether groups are excluded as they would have the opposite surface polarity, retarding emission. Another possible explanation for the NEA zone is that NEA-quenching contaminants introduced by the EC treatment onto the predominantly hydrogenated IC were removed or were never introduced in the NEA zone. HREELS of an EC-treated surface revealed features associated with both hydrocarbon and oxygen-based species over the entire surface. The stripe alone could not be interrogated by HREELS due to the 5×0.5 mm electron beam spot size.

The comparisons presented in this work emphasize the sensitivity to surface chemistry of the diamond χ , which must be controlled in NEA devices. For example, IC and IA regions of EC-treated samples differ in χ from their respective hydrogenated and oxidized analogs, even though they resemble the analogs with respect to LEED, oxygen content, C 1s binding energies, VB photoemission, and band bending. The role of contaminants in controlling χ on the EC-treated samples is suggested by the foreign hydrocarbon and oxygen-based species found with HREELS. As noted above, these contaminants had little effect on band bending. This downward band bending, consistent with *p*-type samples, at-

tracts CBM electrons toward the surfaces. The electrons may escape into vacuum if χ is small enough, as is routinely found for uncontaminated hydrogenated surfaces. For the IC region, however, χ increased 0.3 eV, blocking electron transmission (see Fig. 3). Evidently the contaminants are sufficiently polar to increase the surface dipole, increasing χ . The zone separating the IC and IA regions retains NEA, possibly because it resists water or air modification and repels or eliminates hydrocarbon contamination.

This work was supported in part by the Office of Naval Research and by NASA under the Innovative Research Program (IRP-91-341), Diamond UV Imaging Detectors for Astronomy. The authors acknowledge Mike Owens and Jack Rife for technical support and Trevor Humphreys and Brad Pate for technical discussions.

- ¹A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1989).
- ²P. E. Pehrsson, Paper 245, Proc. of the 187th Mtg. of the Electrochemical Soc., Reno, May 21–26, 1995 (in press).
- ³P. E. Pehrsson and J. E. Butler, Proc. 2nd NIRIM Intl. Symp. Adv. Mat. (ISAM '95), Tsukuba, Japan, March 6–10, 1995, edited by Y. Bando, M. Kamo, H. Haneda, and T. Aizawa, p. 279.
- ⁴P. E. Pehrsson, Paper 246, Proc. of the 187th Mtg. of the Electrochemical Soc., Reno, May 21–26, 1995 (in press).
- ⁵F. J. Himpsel, J. A. Knapp, J. A. VanVechten, and D. E. Eastman, Phys. Rev. B **20**, 624 (1979).
- ⁶B. B. Pate, Surf. Sci. **165**, 83 (1986).
- ⁷R. J. Nemanich, L. Bergman, K. F. Turner, J. van der Weide, and T. P. Humphreys, Physica B **185**, 528 (1993).
- ⁸G. D. Kubiak and K. W. Kolasinski, Phys. Rev. B **39**, 1381 (1989).
- ⁹M. Marchywka, P. E. Pehrsson, D. J. Vestyck, Jr., and D. Moses, Appl. Phys. Lett. **63**, 3521 (1993).
- ¹⁰Harris Corp., 100 Stierli Ct., Suite 106, Mt. Arlington, NJ 07856.
- ¹¹B. D. Thoms, J. N. Russell, P. E. Pehrsson, and J. E. Butler, J. Chem. Phys. **100**, 8425 (1994).
- ¹²B. D. Thoms, M. S. Owens, J. E. Butler, and C. Spiro, Appl. Phys. Lett. **65**, 2957 (1994).
- ¹³R. E. Thomas, R. A. Rudder, and R. J. Markunas, J. Vac. Sci. Technol. A **10**, 2451 (1992).
- ¹⁴B. D. Thoms and J. E. Butler, Surf. Sci. **328**, 291 (1995).
- ¹⁵T. Aizawa, T. Ando, M. Kamo, and T. Sato, Phys. Rev. B **48**, 18 348 (1993).
- ¹⁶H. Nakahata, T. Imai, and H. Fujimori, in *Proceedings of the 2nd International Symposium on Diamond Materials*, 91-8, edited by A. J. Purdes, B. M. Meyerson, J. C. Angus, K. E. Spear, R. F. Davis, and M. Yoder (The Electrochemical Society, Pennington, NJ, 1991), p. 487.
- ¹⁷Y. Mori, Y. Show, M. Deguchi, H. Yagi, H. Yagyū, N. Eimori, T. Okada, A. Hatta, K. Nishimura, M. Kitabatake, T. Ito, T. Hirao, T. Izumi, T. Sasaki, and A. Hiraki, Jpn. J. Appl. Phys. **32**, L987 (1993).
- ¹⁸D. P. Malta, J. B. Posthill, T. P. Humphreys, R. E. Thomas, G. G. Fountain, R. A. Rudder, G. C. Hudson, M. J. Mantini, and R. J. Markunas, Appl. Phys. Lett. **64**, 1929 (1994).