PHYSICAL REVIEW B VOLUME 20, NUMBER 2 15 JULY 1979

Quantum photoyield of diamond(111)—A stable negative-affinity emitter

F. J. Himpsel, J. A. Knapp, J. A. VanVechten, and D. E. Eastman
IBM Thomas J. Watson Research Center, P.O. Box 218, Yorktown Heights, New York 10598

(Received 14 February 1979)

Quantum photoyield and secondary-electron distributions are presented for an unreconstructed diamond (111) surface (type-II*b*, gem-quality blue-white semiconductor). This chemically inert surface exhibits a negative electron affinity, resulting in a stable quantum yield that increases linearly from photothreshold (5.5 eV) to ~20% at 9 eV, with a very large yield of ~40%–70% for $13 \lesssim h\nu \lesssim 35$ eV. For all photon energies, secondary-electron energy distributions show a dominant ~0.5-eV-wide emission peak at the conduction-band minimum ($\Delta_1^{\min} = 5.50 \pm 0.05$ eV above the valence-band maximum Γ_{25}'). In contrast with recent self-consistent calculations [J. Ihm, S. G. Louie, and M. L. Cohen, Phys. Rev. B 17, 769 (1978)], no occupied intrinsic surface states with ionization energies in the fundamental gap (the Fermi level was 1 eV above Γ_{25}') were observed. Likewise, the measured photothreshold ($E_{\text{vac}} - \Gamma_{25}'$) is significantly smaller than calculated (7.0±0.7 eV).

INTRODUCTION

In this paper we present photoemission-quantum yield data and secondary-electron energy distributions for the unreconstructed diamond(111) 1×1 surface. There has been considerable interest in both the bulk[1] and surface properties in recent years, with many band calculations[2,3] and optical studies of bulk properties[4-6] as well as surface and interface state calculations,[3] low-energy electron diffraction (LEED) studies,[7] and photoemission studies.[8-10] However, to our knowledge there have been no photoemission studies of single-crystal surfaces, in particular of semiconducting type-II diamonds which permit photoemission studies, LEED studies, etc., to be made without deleterious charging effects.

For the unreconstructed natural diamond(111) surface, we have found a negative electron affinity, i.e., the vacuum level lies in the fundamental optical gap below the conduction-band minimum $\Delta_1^{\min}$ which has been reported[5] as 5.47 eV above the valence-band maximum Γ_{25}'. This behavior is unusual for a pure covalent solid, e.g., self-consistent pseudopotential calculations[3] for the unrelaxed unreconstructed diamond(111) surface predict a much larger photothreshold, i.e., $\Phi_{\text{th}} \simeq 7 \pm 0.7$ eV above Γ_{25}'. In agreement with the LEED studies of Lurie and Wilson,[7] we have found that the diamond(111) surface is extremely inert to adsorption. This behavior, together with its negative electron affinity, results in type-II*b* diamond(111) having the unusual properties of being a chemically stable semiconducting photoemitter with a large quantum efficiency. In general, negative electron affinities are observed either for wide-gap compounds such as LiF which are insulators, or after complex surface treatments (e.g., Cs plus O on GaAs) which render the surface chemically sensitive.

While the large photothreshold of $\Phi_{\text{th}} = 5.5 \pm 0.05$ eV of diamond(111) precludes its use as a photocathode in the visible and near uv, it has potentially interesting and useful photocathode properties in the vacuum uv, i.e., a stable quantum efficiency of 40%–70% for $12 \lesssim h\nu \lesssim 35$ eV and above. Also, while the use of large cleaved single-crystal diamond surfaces is hardly viable for many applications, the possibility exists for growing epitaxial oriented films of diamond on suitable substrates.[11,12] Such systems offer potential for technologically interesting vacuum-uv photocathodes.

EXPERIMENTAL

The natural (111) surface of a single-crystal blue-white diamond (boron-doped, type-II*b*, about 6 × 5 × 4 mm in size) was studied. The surface was prepared in a manner suggested by Lurie and Wilson,[7] i.e., the crystal was washed ultrasonically in acetone and then mounted in the photoelectron spectrometer. After a ~150 °C bakeout, a sharp unreconstructed 1×1 LEED pattern (at all measured beam energies $25 \lesssim E \lesssim 300$ eV) and angle-integrated photoemission spectra indicative of a rather clean surface were observed. After subsequent *in situ* heating to ~900 °C in the low 10^{-10}-Torr range, the photoemission spectra sharpened slightly without any significant changes and the 1×1 LEED pattern remained unchanged; an Auger spectrum indicated a clean surface (estimated ≲1 at.%

© 1979 The American Physical Society

of O, B, etc., impurities).

Photoemission measurements were made using synchrotron radiation from the 240-MeV storage ring of the University of Wisconsin–Madison and a display-type electron energy analyzer which analyzes all emitted electrons within a 1.8-sr cone (85° full angle).[13] The photon energy resolution was $\lesssim 0.1$ eV and electron energy resolution was typically ~0.15 eV. A LiF transmission filter was used to eliminate higher-order light for $h\nu \lesssim 11.6$ eV. Measurements of absolute quantum yield were performed by comparing the total yield of diamond with those of clean and air-exposed gold photodiodes, and with the fluorescent response of a sodium salicylate film. Calibration was done using the clean Au quantum yield reported by Krolikowski and Spicer[14] for $5 \lesssim h\nu \lesssim 11$ eV and the dirty Au quantum yield reported by Sampson[15] for $10 \lesssim h\nu \lesssim 35$ eV.

RESULTS AND DISCUSSION

Figure 1 shows the quantum yield in the range $5 \lesssim h\nu \lesssim 35$ eV from a natural (111) surface of a semiconducting type-II*b* diamond (boron doped) which exhibits an unreconstructed 1×1 LEED pattern. For comparison, the optical absorption coefficient $\alpha(\nu) = 4\pi\nu k(\nu)/c$ [$k(\nu)$ is the extinction coefficient] as given by the optical constants of Roberts and Walker[6] is also shown in Fig. 1. An indirect absorption edge ($\Gamma'_{25} \rightarrow \Delta_1^{\mathrm{min}}$) of 5.47 eV (the fundamental gap E_{gap}) has been reported.[5] As seen in Fig. 1, the optical absorption is very weak just above the edge and starts to increase for $h\nu \gtrsim 6.5$ eV. In contrast, the quantum yield increases linearly from a photothreshold $\Phi_{\mathrm{th}} = 5.5 \pm 0.05$ eV that is equal to the indirect absorption edge. This behavior signifies the existence of a negative electron affinity, as do the measured energy distributions (to be discussed).

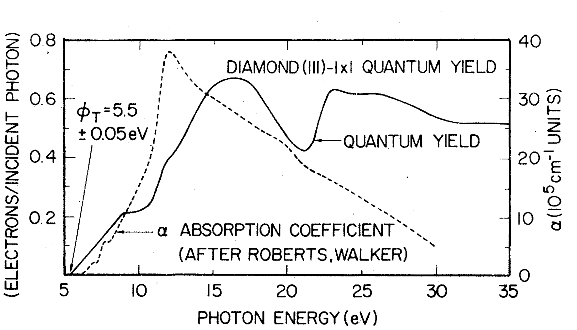

FIG. 1. Quantum photoyield (electrons/photon) of the natural diamond(111) 1×1 surface. The photothreshold $\Phi_{\mathrm{th}} = 5.5 \pm 0.05$ eV is equal to the fundamental optical gap,[4] i.e., diamond(111) 1×1 has a negative electron affinity. For comparison, the optical-absorption coefficient spectrum (after Roberts and Walker[6]) is shown.

In Fig. 1, the quantum yield is seen to increase nearly linearly from photothreshold to ~20% at $h\nu \simeq 9$ eV, and then increase to ~40%–70% throughout the range $12 \lesssim h\nu \lesssim 35$ eV. Spectral structures are seen in the quantum yield near 8.5, 12, and ~22 eV that approximately correlate with structures in the absorption coefficient spectrum $\alpha(\nu)$ and the corresponding imaginary part of the dielectric constant $\epsilon_2(\nu)$ (i.e., structures are seen at 7.3, 7.8, 12.2, and 23 eV in ϵ_2).[6] However, the line shape of the quantum yield curve is very different from the $\alpha(\nu)$ and $\epsilon_2(\nu)$ curves. The strong increase in quantum yield just above threshold and the large yield at higher photon energies are due to a large effective escape depth for secondary electrons resulting from a combination of the negative electron affinity together with the large (5.5-eV) band gap.

Additional information on the secondary-emission process is given by the photoemission energy distribution curves (EDC's) for $h\nu = 12$ and 60 eV shown in Fig. 2. These EDC's show the spectral distribution of the secondary electrons which dominate the quantum yield. The energy scale is plot-

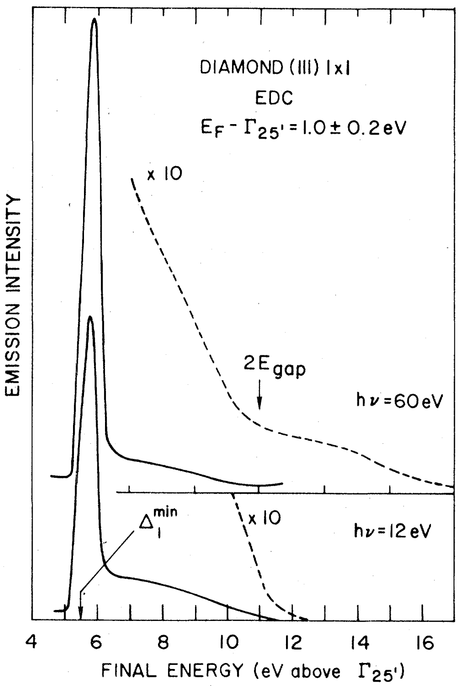

FIG. 2. Photoemission energy distribution curves (EDC's for diamond(111) 1×1 at $h\nu = 12$ and 60 eV showing characteristic secondary-electron-emission spectra (see text). Emission is observed down to the conduction-band minimum Δ_1^{min} due to the negative electron affinity.

ted relative to the valence-band maximum Γ'_{25}; actually, the EDC's were measured relative to the Fermi level E_F and the position of E_F relative to Γ'_{25} was separately determined ($E_F - \Gamma'_{25} = 1.0 \pm 0.2$ eV; this value is extrinsic and could vary for samples with different doping or differently prepared surfaces). The EDC's also directly show the existence of a negative electron affinity since emission is measured for all energies down to the conduction band minimum Δ_1^{min}.

The EDC's in Fig. 2 show two spectral features, a dominant ~0.5-eV-wide (full width at half maximun) peak of secondaries centered just at or above Δ_1^{min} and a broad triangularlike spectral feature which extends from Δ_1^{min} to ~10 eV above Γ'_{25}. The sharp peak—whose shape is essentially independent of photon energy for $h\nu \gtrsim 6$ eV—is due to quasi thermalized secondaries in the lowest conduction band[16] which has a relatively flat minimum centered at Δ_1^{min}. The width of this peak is due in part to our experimental resolution (~0.15 eV), and to the intrinsic spectral width due to phonon scattering ($\hbar\omega_{\text{opt}} \sim 170$ meV for optical phonons), but also could be due in part to inhomogeneities, i.e., inhomogeneous band bending. Negligible charging was observed for all photoemission and LEED measurements for currents $\lesssim 10^{-5}$ A, including LEED measurements down to ~25 eV.

The spectral shape of the broad secondary-emission feature in Fig. 2 is essentially independent of photon energy for $h\nu \gtrsim 12$ eV. Its upper edge at ~10 eV corresponds to a final energy $2E_{\text{gap}}$ above Γ'_{25}. For electron energies above this upper edge, electron-electron scattering occurs which results in a relatively short effective escape depth and small emission intensity. For energies below this edge, only electron-phonon (plus impurity) scattering can occur, with a corresponding large effective escape depth and large emission intensity.[17]

A remarkable feature of this natural (111) diamond surface is its chemical inertness and subsequent stable photoemission characteristics. The quantum yield curve for the unheated crystal (simply washed in acetone and baked out at ~150 °C) was essentially identical to that in Fig. 1, which was taken after *in situ* heating to ~900 °C. EDC's for the unheated crystal also gave evidence of relatively slight contamination, i.e., primary photoemission structures due to direct transitions were seen. These spectral features became somewhat sharper after the 900 °C heat treatment, but did not significantly change.

In our photoemission studies of diamond(111) 1×1 to date (primarily angle-integrated measurements), no evidence of occupied intrinsic surface states in the fundamental gap has been found. This is in interesting contrast with both self-consistent surface-state calculations for the ideal diamond-(111) surface by Ihm *et al.*[3] and with past observations of such intrinsic surface states on Si(111) 2×1 and Ge(111) 2×1 surfaces.[18] Namely, for the ideal unrelaxed diamond(111) surface, a sharp band of dangling bond intrinisic surface states has been predicted[3] at ~1.8 eV above Γ'_{25}. If the surface relaxes (as is most likely), one can expect these states to move to lower energy. However, it is very surprising that a relaxation which retains the 1×1 surface unit cell (as seen with LEED) can cause the intrinsic surface states to move downward by $\gtrsim 2$ eV. One possibility was that the intrinsic surface states near the gap for our sample were removed by a fraction of a monolayer of an adsorbate (e.g., O, B, H, etc.); we have looked for such contaminants using both Auger spectroscopy and photoemission spectroscopy for $5 \lesssim h\nu \lesssim 50$ eV and were unable to find any adsorbate which could account for such a behavior. Another possibility is that carbon atoms in the surface layer are rearranged in some manner as to greatly modify the intrinsic surface states while not forming a superlattice that is detectable with LEED (e.g., disordered layer). A third possibility is that surface states are sufficiently localized and the dielectric screening sufficiently small that large correlation effects are present, i.e., the measured ionization energy for the localized state is larger than the corresponding calculated one-electron ground-state energy. If so, this could result in surface-state ionization energies being degenerate with the upper bulk valence-band state energies, and thus being harder to detect. However,such states should be relatively sharp and, by comparison with Si(111) and Ge(111),[18] should be detectable. Additional work is in progress to further search for surface states and to understand this interesting preliminary observation, including angle-resolved photoemission studies and controlled adsorbate studies.

ACKNOWLEDGMENTS

We wish to thank Dr. C. Phaal, Dr. F. A. Raal, Mr. G. C. McCallum, and the DeBeers Industrial Diamond Division Ltd. for providing the high-quality, type-II*b*, semiconducting diamonds used in these experiments. Also, the Synchrotron Research Center, Stoughton, Wisconsin is acknowledged for their usual able assistance.

[1] *Physical Properties of Diamond,* edited by R. Berman (Clarendon, Oxford, 1965).

[2] G. S. Painter, D. E. Ellis, and A. R. Lubinsky, Phys. Rev. 4, 3610 (1971).

[3] J. Ihm, Steven G. Louie, and Marvin L. Cohen, Phys. Rev. B 17, 769 (1971).

[4] H. R. Philipp and E. A. Taft, Phys. Rev. 127, 159 (1962).

[5] C. D. Clark, P. J. Dean, and P. V. Harris, Proc. R. Soc. A 277, 312 (1964).

[6] R. A. Roberts and W. C. Walker, Phys. Rev. 161, 730 (1967).

[7] P. G. Lurie and J. M. Wilson, Surf. Sci. 65, 453 (1977).

[8] R. G. Cavell, S. P. Kowalczyk, L. Ley, R. A. Pollak, B. Mills, D. A. Shirley, and W. Perry, Phys. Rev. B 7, 5313 (1973).

[9] F. R. McFeely, S. P. Kowalczyk, L. Ley, R. G. Cavell, R. A. Pollak, and D. A. Shirley, Phys. Rev. B 9, 5268 (1974).

[10] S. Evans and J. M. Thomas, Proc. R. Soc. A 353, 103 (1977).

[11] S. Aisenberg and R. W. Chabot, J. Vac. Sci. Technol. 10, 104 (1973).

[12] E. G. Spencer, P. H. Schmidt, D. C. Joy, and F. J. Sansalone, J. Appl. Phys. 29, 118 (1976).

[13] D. E. Eastman, F. J. Himpsel, and J. A. Knapp, Phys. Rev. Lett. 40, 1514 (1978).

[14] W. F. Krolikowski and W. E. Spicer, Phys. Rev. B 1, 478 (1970).

[15] James A. R. Samson, *Techniques of Vacuum Ultraviolet Spectroscopy* (Wiley, New York, 1967).

[16] L. W. James and J. L. Moll, Phys. Rev. 183, 740 (1969).

[17] D. E. Eastman, *Techniques of Metals Research VI,* edited by E. Passaglia (Interscience, New York, 1972), pp. 413–479.

[18] D. E. Eastman and W. D. Grobman, Phys. Rev. Lett. 28, 1378 (1972).