Applied Physics Letters

Observation of a negative electron affinity for boron nitride

Cite as: Appl. Phys. Lett. **67**, 3912 (1995); https://doi.org/10.1063/1.115315
Submitted: 14 June 1995 • Accepted: 14 October 1995 • Published Online: 05 August 1998

M. J. Powers, M. C. Benjamin, L. M. Porter, et al.

AIP Publishing

Observation of a negative electron affinity for boron nitride

M. J. Powers, M. C. Benjamin, L. M. Porter, R. J. Nemanich,[a] R. F. Davis, and J. J. Cuomo
Department of Physics and Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695-8202

G. L. Doll and Stephen J. Harris
Physical Chemistry Department, General Motors R&D Center, Warren, Michigan 48090-9055

(Received 14 June 1995; accepted for publication 14 October 1995)

This study reports UV-photoemission (UPS) measurements made on boron nitride crystals and thin films. The materials examined are commercial grade *c*-BN powder and thin films of BN deposited with ion beam assisted e-beam evaporation and laser ablation. The thin film samples examined exhibited varying amounts of sp^3 (cubic) and sp^2 (hexagonal, amorphous) bonding as determined by FTIR measurements. The UPS measurements displayed the spectral distribution of the low energy photoemitted electrons and the total energy width of the spectra. These characteristics can be related to the electron affinity. The measurements on several of the BN powder and thin film samples revealed features in the emission spectra which are indicative of a negative electron affinity (NEA) surface. © *1995 American Institute of Physics.*

The electron affinity of a semiconductor is the difference between the vacuum energy level and the conduction band minimum level. The phenomenon of a negative electron affinity (NEA) occurs when the conduction band minimum energy lies above the vacuum energy level. Any electron promoted into the conduction band then has enough energy to escape into vacuum. This phenomenon has potential for application in electron emission devices with unique properties. Currently, NEA photocathodes are utilized in many photodetector designs but are easily poisoned by contamination. This disadvantage has impeded development of practical NEA vacuum electronic devices in other applications such as cold cathode emitters.[1]

The presence of a NEA can be determined by ultraviolet photoemission spectroscopy (UPS).[2–4] This technique involves directing $h\nu=21.2$ eV photons (He I resonance line) onto the sample surface and energy analyzing the emitted photoelectrons. The UPS technique is typically used to profile the valence band (VB) electronic states. As such, most UPS studies present spectra of only the most energetic emitted electrons. Scattered and secondary electrons will be emitted at the lower kinetic energies in the spectra. For a semiconductor with a NEA surface, a distinctive peak may be observed at the lowest kinetic energy in the spectra. This low energy feature is due to the large number of electrons that have (quasi) thermalized to the conduction band minimum and still have enough energy to escape into vacuum. A second indication of a NEA is that the width of the UPS spectra is $W=h\nu-E_g$, where W (the width of the emission spectrum) extends from the low energy limit to the VB maximum and E_g is the band gap of the material. In contrast, for materials with a positive electron affinity, the UPS measurements follow the relation $W=h\nu-E_g-\chi$, where χ is the electron affinity.

Recently, aluminum nitride (AlN) was shown to exhibit a NEA.[5] The AlN previously shown to be NEA has been exposed to ambient demonstrating the potential ruggedness of these NEA surfaces. Similarly, boron nitride (BN) was identified as an excellent candidate for also having a NEA surface. It has also been shown that cubic BN (*c*-BN) can be *p*-type and *n*-type doped with Be and Si, respectively.[6] In this study all samples were examined "as is" after being transported in air. BN samples prepared by three different methods were studied in this work; commercial grade *c*-BN powder,[7] and BN thin films deposited with ion beam assistance by e-beam evaporation[8] and pulsed laser deposition.[9]

Figures 1(a) and 1(b) show scanning electron microscopy (SEM) images of *c*-BN crystals deposited on highly oriented pyrolytic graphite (HOPG). The crystals were electrophoretically deposited[10] using a monocrystalline *c*-BN powder[7] with crystal sizes less than 0.5 μm. To prepare these samples, 100 mg of the *c*-BN powder was mixed with 100 ml of ethyl alcohol and dispersed into a uniform solution. Graphite was chosen for the deposition electrodes due to the conductive nature and the low photoemission yield of graphite in UPS measurements. The two electrodes were suspended in the solution approximately 1 cm from each other and a potential of 8 V was applied between them for 8 min. The coverage is estimated from the SEM images to be ~80%. A 10 mm×10 mm piece of the sample was cut and mounted for the photoemission measurements.

The substrates on which the e-beam BN thin films were deposited were on-axis (100) single crystal, B-doped Si ($\rho=25-45\ \Omega$ cm). Cleaning consisted of a 10 min oxide etch in 10% HF followed by heating to 700 °C for 15 min in ultrahigh vacuum. The substrates were subsequently transferred *in vacuo* to the deposition system.

The e-beam films were deposited in a UHV system (base pressure $<5\times10^{-10}$ Torr) onto substrates heated to 400 °C. Boron was deposited at a rate of 0.5 Å/s by electron beam evaporation from a solid source. Simultaneously a 3 cm

---

[a] Electronic mail: robert_nemanich@ncsu.edu

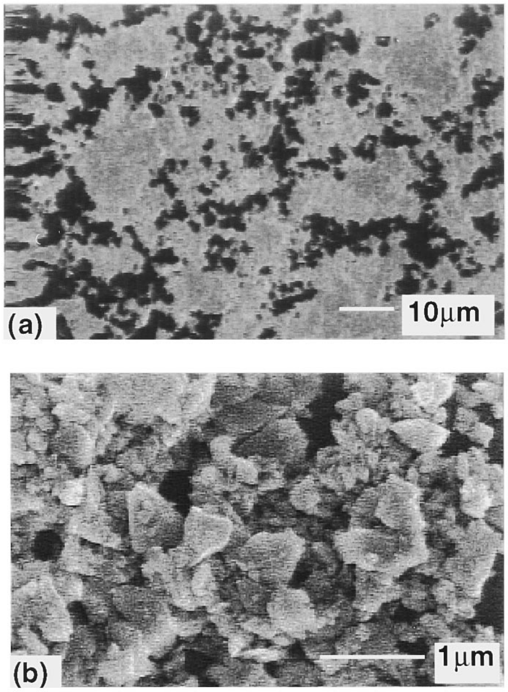

FIG. 1. SEM images of (a) graphite substrate (dark areas) covered with *c*-BN powder (light areas) and (b) magnified image of *c*-BN crystals on same substrate.

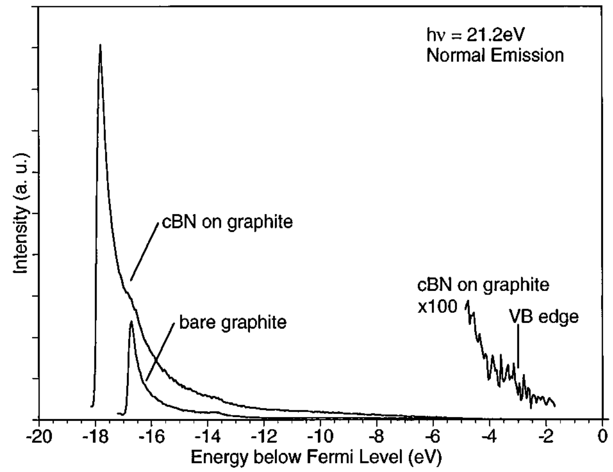

FIG. 2. UV photoemission spectra of *c*-BN powder on graphite and bare graphite. Samples were biased at −2 V to overcome the work function of the energy analyzer. The spectral widths are consistent with a band gap of 6.2±0.3 eV for the *c*-BN and a work function of 4.4±0.3 eV for the graphite. The spectra are displayed at the same scale.

Kaufman-type ion source was operated with a beam energy of 500 eV to assist the deposition. N_2 and Ar flowed at 1.5 sccm each through the ion source during deposition. The deposition system and procedure are described in detail elsewhere.[8]

The third set of BN films were grown by pulsed laser deposition on Si(100) substrates. In this technique, a KrF excimer laser is focused onto a hexagonal BN target. The laser operates at 248 nm, a 22 ns pulsewidth, and 500 mJ of energy per pulse. The laser initiates a plasma directed normal to the surface of the target from which B and N atoms, ions, and molecules are jettisoned and subsequently deposit on the substrate. The process is conducted in approximately 100 mT of N_2 gas which helps promote stoichiometry in the film.[9] The BN films grown in this way are predominantly sp^2-bonded and have a hexagonal crystal structure.[11]

The BN thin films were analyzed in transmittance mode by Fourier-transform infrared spectroscopy (FTIR) to determine the BN phases. The spectrum obtained from a bare Si substrate was subtracted from all spectra obtained from the BN/Si samples. Tetragonally coordinated sp^3-bonded cubic BN exhibits a transverse optical mode absorption peak at 1075 cm $^{-1}$. Hexagonal and amorphous BN are indistinguishable in the FTIR spectra as both are made up of threefold coordinated sp^2-bond types characterized by a primary absorption peak at 1367 cm^{-1} and a secondary absorption peak at 783 cm $^{-1}$.[12,13]

The UPS chamber has a base pressure of 2×10^{-10} Torr. A differentially pumped helium resonance lamp is used to provide 21.2 eV (He I line) UV light on the sample. The additional helium increases the background pressure during measurements up to 2×10^{-9} Torr. A 50 mm radius hemispherical energy analyzer is used to measure the energy spectrum of the photoemitted electrons. The apertures used in the analyzer for this study give a 0.15 eV energy resolution and a 2° angular resolution. The effective acceptance area of the analyzer is a spot approximately 2 mm in diameter on the sample. The sample to be examined is fastened onto a molybdenum sample holder with tantalum wire. Biasing of the sample holder up to several volts can be done to overcome any difference between the work function of the analyzer and the sample. UPS measurement of a clean molybdenum surface with no sample bias (i.e., grounded) is used to determine the Fermi energy level of the system.

UPS measurements of the *c*-BN powder sample are shown in Fig. 2. A sharp feature at the higher binding energies (i.e., lowest kinetic energy) is clearly visible indicating that the electrons that have thermalized to the conduction band minimum are escaping into vacuum. The feature is similar in sharpness to features observed in diamond.[2–4,14] The *c*-BN coated sample was biased up to 2 V to reveal the full width of the electron energy spectrum. The width of the spectrum is determined by linearly extrapolating the left and right sides of the curve to zero. The very low signal which continues up to the Fermi level is attributed to the graphite. Auger electron spectroscopy (AES) revealed the presence of C along with B and N. Since the probing area and depth of AES and UPS are similar, some graphite photoemission signal is expected in the UPS data. A weak oxygen feature (~1 ML) was also observed in the AES spectra, and no other impurities were observed below 600 eV.

In an effort to separate the *c*-BN powder and graphite signals a piece of bare HOPG was examined with UPS. As can be seen from Fig. 2 the spectra from the bare HOPG is significantly different from the *c*-BN powder coated sample. The overall magnitude of the photoemission signal from the *c*-BN powder surface is about 5× greater than from the bare graphite surface. The valence band spectrum of the bare HOPG sample is rather featureless in comparison with pre-

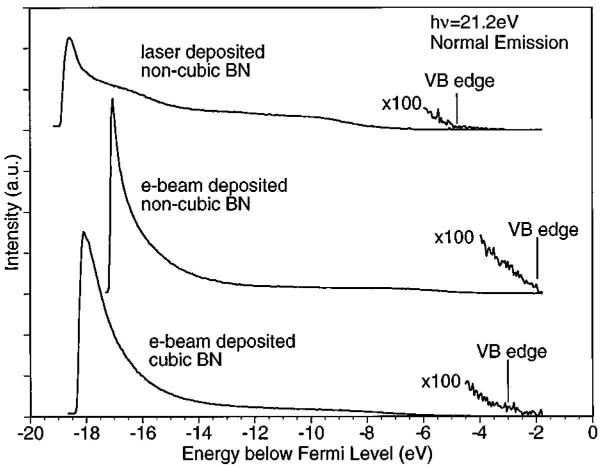

FIG. 3. UV photoemission spectra of e-beam deposited cubic and noncubic BN, and laser deposited noncubic BN. Samples were biased at −3 V to overcome the work function of the energy analyzer. The spectral widths of the e-beam deposited samples are consistent with band gaps of 5.8±0.3 eV for the cubic and 6.0±0.3 eV for the noncubic sample. The spectrum of the laser deposited sample is not consistent with a NEA. The spectra are displayed at the same scale.

viously reported spectra of graphite.[15] The final state feature at ~13.7 eV below E_f is, however, just discernible. We attribute the featureless spectra to the air exposed and rough, processed surface of the sample. However, the width of the spectra is consistent with the 4.4 eV work function of graphite. The band gap of cubic BN has been reported as $E_g = 6.4 \pm 0.5$ eV.[16] Thus, if the material has a NEA, the width of the spectrum should be $h\nu - E_g = 14.7 \pm 0.5$ eV. Extrapolating the intensities of the c-BN powder spectrum to zero on both sides of the spectra yield a width of 15.0±0.3 eV, corresponding to a band gap of 6.2±0.3 eV. The Fermi level is found at 3.0 eV above the VB edge which is about $E_g/2$ indicating that the c-BN powder is essentially intrinsic.

A NEA was observed for most of the thin films deposited with the e-beam method. Since the reported band gap of c-BN is larger than diamond while the band gap of h-BN is less, it might be expected that the c-BN would exhibit a NEA and the h-BN would not. However, investigations of numerous samples with various thicknesses did not support this hypothesis. Figure 3 shows typical spectra from e-beam deposited thin films where both the c-BN and the h-BN samples appear to have the characteristic strong emission of a NEA. We note that the AES of all the thin film samples showed oxygen and carbon surface impurities that are likely due to the long ambient exposures prior to the UPS measurements. A few samples of both c-BN and h-BN did not display the strong emission typical of NEA behavior, possible explanations for these results are discussed below. The widths of the spectra in Fig. 3 correspond to band gaps of 5.8±0.3 eV and 6.0±0.3 eV for the c-BN and h-BN, respectively. This was unexpected since c-BN is generally observed to have a larger band gap than the noncubic phase of BN.[16,17]

Several laser deposited samples which showed no detectable cubic BN in FTIR were examined with UPS. A typical spectrum from the laser deposited samples is also shown in Fig. 3. The magnitude of the peak emission signals was generally lower than that from the other surfaces studied. While the spectrum in Fig. 3 shows emission extending to low energies, the spectral width would correspond to a band gap of 7.2±0.3 eV which is too large to be consistent with reported values for noncubic BN (3.8–6.2 eV).[17] Alternatively, if we assume a band gap of 5 eV, the measurement would indicate a positive electron affinity of 2.2 eV.

We note that the analysis presumes that the surface band gap is the same as the bulk. The presence of filled surface states could modify the surface band gap, but we have not identified such states in any spectra.

The electron affinity is strongly affected by the surface termination which may be the cause of the differing results on the deposited films. A thin layer of c-BN may be present on the surface of a hexagonal sample (or visa–versa) and remain undetected by the FTIR measurements due to the low signal. Some samples were observed to crack from internal stresses in the BN film which would certainly give rise to nonuniform surface effects. Since the samples have been exposed to atmosphere prior to the UPS measurements, environmental contaminants may also be responsible for altering the surface dipole which determines the electron affinity. Further study is needed in order to establish the surface conditions which favor a NEA on BN.

We gratefully acknowledge Eric Watko for performing FTIR measurements. This work was supported in part by the Office of Naval Research.

[1] B. F. Williams and R. E. Simon, Appl. Phys. Lett. **14**, 214 (1969).
[2] F. J. Himpsel, J. A. Knapp, J. A. van Vechten, and D. E. Eastman, Phys. Rev. B **20**, 624 (1979).
[3] B. B. Pate, M. H. Hecht, C. Binns, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. **21**, 364 (1982).
[4] B. B. Pate, Surf. Sci. **165**, 83 (1986).
[5] M. C. Benjamin, C. Wang, R. F. Davis, and R. J. Nemanich, Appl. Phys. Lett. **64**, 3287 (1994).
[6] R. H. Wentorf, Jr., J. Chem. Phys. **36**, 1990 (1962).
[7] Borazon BMP-1 (0–0.5 μm) from GE Superabrasives Inc., Worthington, OH, 43085.
[8] D. J. Kester, K. S. Ailey, D. J. Lichtenwainer, and R. F. Davis, J. Vac. Sci. Technol. A **12**, 3074 (1995).
[9] G. L. Doll, J. A. Sell, L. Salamanca-Riba, and A. K. Ballal, in Laser Ablation for Materials Synthesis, edited by D. C. Paine and J. C. Bravman (Materials Research Society Proceedings Pittsburgh, PA 1990), Vol. 191, pp. 55–60.
[10] J. J. Cuomo and G. R. English, IBM Tech. Disclosure Bull, **321**, 321100 (1991).
[11] G. L. Doll, M. C. Militello, S. J. Simko, A. K. Ballal, and L. Salamanca-Riba, in *Silicon Carbide and Related Materials*, edited by M. G. Spencer, R. P. Devaty, J. A. Edmond, M. Assif Khan, R. Kaplan, and M. Rahman [Instit. Phys. Conf. Ser. No. 137, Philadelphia, PA (1994)], pp. 449–452.
[12] R. Geick, C. H. Perry, and G. Rupprecht, Phys. Rev. **146**, 543 (1966).
[13] P. J. Geilisse, S. S. Mitra, J. N. Pendl, R. D. Griffis, L. C. Mansur, R. Marshall, and E. A. Pascoe, Phys. Rev. **155**, 1039 (1967).
[14] J. van der Weide and R. J. Nemanich, Appl. Phys. Lett. **62**, 1878 (1993).
[15] P. M. Williams, in *Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy*, edited by D. Briggs (Heyden & Son, Philadelphia, PA, 1978), pp. 313–340.
[16] V. Laurence, G. Demazeau, and J. Etourneau, Mater. Sci. Eng. **10**, 149 (1991).
[17] S. P. S. Arya and A. D'Amico, Thin Solid Films **157**, 267 (1988).