



UPS of Boron-Sulfur Co-Doped, n-Type Diamond

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The band structure of n-type diamond samples co-doped with boron and sulfur was studied using ultraviolet photoelectron spectroscopy (UPS) and Mott-Schottky analysis. The results show that the Fermi energy of the co-doped diamond is about 0.8-1.9 eV above the Fermi level of boron-doped diamond. The electron affinities of the samples ranged from -0.7 to -1.4 eV as evidenced by UPS. These results provide support for the presence of an acceptor impurity band within the bandgap region of the co-doped diamond samples.

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Boron doping of diamond for p-type conductivity has been extensively studied.¹⁻³ However, n-type doping of diamond still remains a challenge. Exploratory studies for potential n-type dopants in diamond have focused mainly on group I and group V elements.⁴⁻¹⁴

Nishitani-Gamo *et al.* were the first researchers to indicate that sulfur doping causes n-type conductivity in diamond.¹⁵ They reported promising values for the activation energy (0.38 eV) and the room temperature Hall mobility ($597 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) for sulfur-doped diamond films grown on (100) substrates. Later, Kalish *et al.*¹⁶ showed that these sulfur-doped samples contained boron and were p-type. Eaton *et al.*^{17,18} demonstrated that sulfur was incorporated into diamond in measurable concentrations only in the presence of boron, and n-type conductivity was achieved only when relatively lower quantities of boron were used. The n-type conductivity of the samples was confirmed using Hall measurements, scanning tunneling spectroscopy (STS), thermoelectric power measurements, and Mott-Schottky analysis. STS of the samples in air using Pt-Ir tips showed that the co-doped samples have an n-type rectifying behavior.¹⁸ The co-doped (100) diamond samples showed an approximate Hall mobility value of $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and a sheet carrier concentration of $5 \times 10^{12} \text{ cm}^{-2}$ with activation energies of 0.05-0.12 eV.¹⁸ However, all the above techniques failed to resolve the exact band structure of the co-doped samples.

In this paper, ultraviolet photoelectron spectroscopy (UPS) is used to characterize the band structure of co-doped diamond samples. The UPS results along with Mott-Schottky analysis are used to determine the position of the Fermi energy relative to the bandedges in the co-doped diamond samples both on the electrochemical and the vacuum scales. Based on the results, a possible model for the observed n-type conductivity in the co-doped diamond samples is proposed and discussed.

Experimental

Co-doped diamond films were grown homoepitaxially on high pressure, high temperature synthetic (HPHT) (100) diamond samples using an AStEX microwave plasma reactor. Co-doping was performed using H₂S and trimethylboron (TMB) as sulfur and boron doping additives during diamond growth using methane and hydrogen feed gases. The procedures for co-doping and Mott-Schottky analysis are described in detail elsewhere.^{17,18} Mott-Schottky analysis is performed using a platinum wire as counter electrode and a standard calomel electrode (SCE) as the reference in a 0.5 M H₂SO₄ electrolyte solution at room temperature. The feed gas compositions used for the growth of the samples in this study are summarized in Table I. All samples were grown using a microwave power of 1000 W. The pressure and substrate temperature were 25 Torr and 750°C,

respectively. The first four samples listed in Table I are analyzed using UPS. Mott-Schottky analysis was extensively studied for various co-doped diamond samples, and the data was presented earlier.^{17,18} Here, the Mott-Schottky data for the last two samples listed in Table I are presented and analyzed.

UPS characterization of the co-doped samples was performed using a multichamber, ultrahigh vacuum (UHV) surface science facility (VG Scientific, England/RHK Technology, MI, USA) comprising of a 150 mm radius CLAM4 hemispherical analyzer and a differentially pumped helium discharge lamp. The ultimate resolution of the UPS data is limited by the natural linewidth of the excitation source at ~0.1 eV. Samples were mounted onto copper holders using copper tape. All spectra were recorded using normal emission and at a constant analyzer energy of 2.5 eV. The surface of the sample was grounded to negate any charging effects during the photoelectron spectra acquisition. The copper holder surface was sputter-cleaned using a 5 keV Ar ion beam and was used as the reference. Following a method described by Diederich *et al.*¹⁹ spectra were also obtained using a 9.0 V negative bias applied to the sample. As indicated in Ref. 19, the application of a 9.0 V negative bias helped overcome the work function of the spectrometer and increased the secondary emission.

Results and Discussion

A typical He(I) (energy = 21.2 eV) UPS spectrum of the sample UPS1, obtained under no applied bias, is presented in Fig. 1. The kinetic energy (KE) scale is referenced w.r.t the standard copper surface by adjusting the Fermi onset on the copper reference spectra to 21.2 eV. Nickel surface was also investigated as a reference, and the results were identical. The position of the vacuum cutoff (E_{VAC}) on the KE scale is determined from the reference spectra obtained using the standard copper surface. The zero of the KE scale of the spectra shown in Fig. 1 corresponds to the Fermi level position (ϵ_{F}) w.r.t E_{VAC} within the band diagram.¹⁹ The relative position of E_{VAC} w.r.t ϵ_{F} gives the work function of the sample.

The procedure for locating the conduction band minimum (CBM) on UPS spectra depends on whether the electron affinity (EA) of a diamond surface is negative or positive. This can be determined by the fact that negative electron affinity (NEA) samples exhibit a stronger emission, than positive electron affinity (PEA) samples and also a sharp shoulder in the low KE region. For NEA samples, the vacuum cutoff lies below the CBM and electrons thermalizing from the conduction band easily escape into vacuum. These electrons appear in the spectrum as a sharp peak in the low kinetic energy part of the spectrum.^{19,20} All four samples listed in Table I showed NEA behavior. In comparison, the oxidized surface of another (100) diamond sample clearly exhibited PEA behavior. The UPS spectrum obtained for the oxidized diamond sample is not included here. The low KE portion of the spectrum for one sample, UPS1, is magnified to demonstrate the sharp shoulder characteristic of the NEA behavior. See the inset in Fig. 1. The relative location of

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Table I. Summary of feed gas compositions used for depositing the co-doped diamond films on HPHT synthetic diamond substrates.

Sample	Orientation	Methane concentration in feed gas (%)	S/C _{feed} (ppm)	B/S _{feed} (ppm)	Film thickness (μm)
UPS 1	(100)	0.25	100	100,000	0.35
UPS 2	(100)	0.25	100	100,000	0.3
UPS 3	(100)	1	3,750	1,250	3
UPS 4	(100)	1	500	75,000	4.2
MS1	(110)	0.125	1,600	25	2.00
MS2	(110)	0.125	2,400	100,000	14

CBM w.r.t the ϵ_F on the KE scale of the spectra from the NEA samples can be determined by extrapolating the NEA peak to zero intensity with an error of 0.1 eV.^{21,22} For the spectrum in Fig. 1, E_{VAC} and the CBM are located at energies of 2.7 and 4.1 eV, respectively, when referenced to ϵ_F .

Theoretically, the position of the valence band maximum (VBM) relative to ϵ_F can also be obtained independently by extrapolating the VBM peak on the high KE part of the spectra to zero intensity. The high KE part of the spectrum could give better spectral resolution of the valence band, if obtained using He(II) radiation (energy = 40.8 eV). However, the determination of the position of the VBM relative to ϵ_F could not be accomplished because of interference from He(I) related photoexcitation. As an alternative, the position of the VBM relative to ϵ_F may be determined by subtracting the (CBM- ϵ_F) value from the known bandgap value of 5.5 eV for diamond.¹⁹

The UPS spectra for all samples were also obtained under an applied negative bias of 9.0 V. This study is done to confirm the occurrence of the sharp shoulder on the low KE part of the spectra is only due to the NEA behavior of the samples. Upon applying the negative bias, NEA samples exhibited a strong increase in the secondary electron emission while retaining the sharp shoulder in the low KE region. A representative spectrum for sample, UPS3, obtained with an applied bias of -9.0 V is compared with that obtained using no applied bias in Fig. 2a. The ϵ_F onsets in both spectra have been fixed to 21.2 eV on the KE scale by referencing to copper as shown in Fig. 2b. The relative positions of E_{VAC} and CBM w.r.t ϵ_F are located at 1.9 and 3.3 eV, respectively, as shown in Fig. 2a. Using a bandgap value of 5.5 eV, the position of VBM is determined to be 2.2 eV w.r.t to ϵ_F .

Using the above procedure as illustrated in Fig. 1 and 2, the band diagrams of all four samples have been constructed and presented in Fig. 3. The band diagram data show that the EA values of the four samples varied from -0.7 to -1.4 eV. These EA values are similar to the values reported in the literature, -0.9 eV for hydrogen terminated undoped diamond and -1.0 eV for hydrogen terminated boron-doped diamond. In comparison, the EA value for oxidized diamond is about +1.0 eV.²³ These results also support earlier studies indicating that sulfur should have only a minor effect on the EA

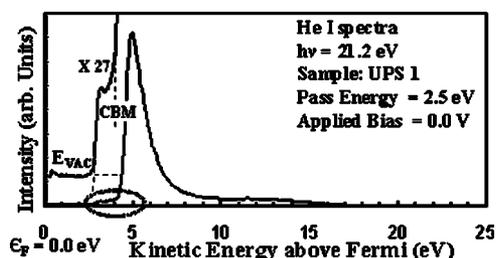


Figure 1. He(I) spectra of co-doped diamond sample UPS1, obtained using no applied bias. The energies of the vacuum cutoff and the CBM relative to Fermi energy are indicated in the figure.

of diamond. Sulfur termination causes a 0.3 eV increase in the work-function compared to hydrogen termination for silicon, and a change of about ± 0.3 eV for III-V semiconductors.²⁴⁻²⁷ Also, Miller²⁸ showed that the thiol functionalization causes only 0.1-0.2 eV decrease in the work function compared to hydrogen-termination for diamond surfaces.

The results also show that the ϵ_F is located closer to the VBM than the CBM in all the samples analyzed. The co-doped samples show the Fermi level to be 1.1-2.2 eV above VBM compared to only 0.3 eV reported for boron-doped samples.¹⁹ Another independent confirmation of this result comes from the Mott-Schottky data for the co-doped samples. Here, representative Mott-Schottky plots of C^{-2} vs. E (where, C is the measured capacitance at the applied voltage, E) for samples MS1 and MS2 are shown in Fig. 4a and b, respectively. The negative slope of the data in Fig. 4a indicates the presence of acceptors, and from the slope the acceptor concentration, N_A , is calculated to be $8.5 \times 10^{21} \text{ cm}^{-3}$. The data in Fig. 4b show a positive slope indicating the presence of donors. The calculated average donor concentration, N_D , was $2 \times 10^{21} \text{ cm}^{-3}$. The flatband potential is determined by the intercept of the best-fit straight line of the data with the voltage axis. The electrochemical scale can be converted to the vacuum scale through

$$qE = 4.44 + \epsilon \quad [1]$$

where E is the electrode potential vs. the standard hydrogen electrode (SHE), ϵ is the electron energy, and $q = -1$ is the charge on

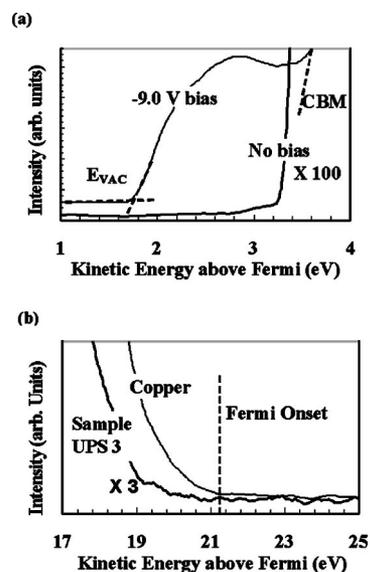


Figure 2. (a) Low KE region of the He(I) spectra of co-doped diamond sample UPS3 showing the increase in intensity with applied negative bias. The energies of the vacuum cutoff and the CBM relative to Fermi energy are indicated. (b) Fermi onset feature of the sample UPS3 and the reference copper surface obtained using an applied bias of -9.0 V. The KE energy scale is adjusted by fixing the Fermi energy of copper to 21.2 eV as shown.

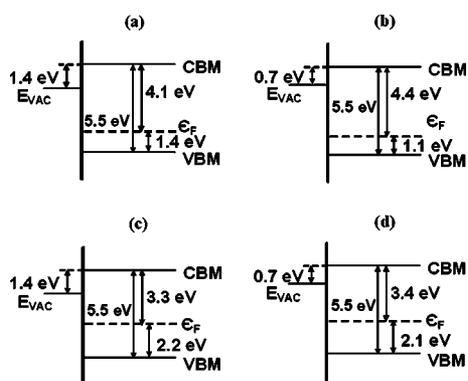


Figure 3. Band diagrams of the co-doped diamond samples obtained using a known value of 5.5 eV for the bandgap of diamond. (a) and (b) Band diagrams of sample UPS1 and UPS2, and (c) and (d) band diagrams of the samples UPS3 and UPS4.

an electron. The Mott-Schottky results showed that the Fermi level for sulfur-doped diamond is only 1-1.5 eV above the Fermi level for boron-doped diamond on the electrochemical scale as illustrated in Fig. 4b. The UPS results are in agreement with the fact that the Fermi level for co-doped diamond samples is located about 0.8-1.9 eV above that observed for boron-doped diamond. Despite Fermi level being in the range of p-type acceptors, electrical and electro-

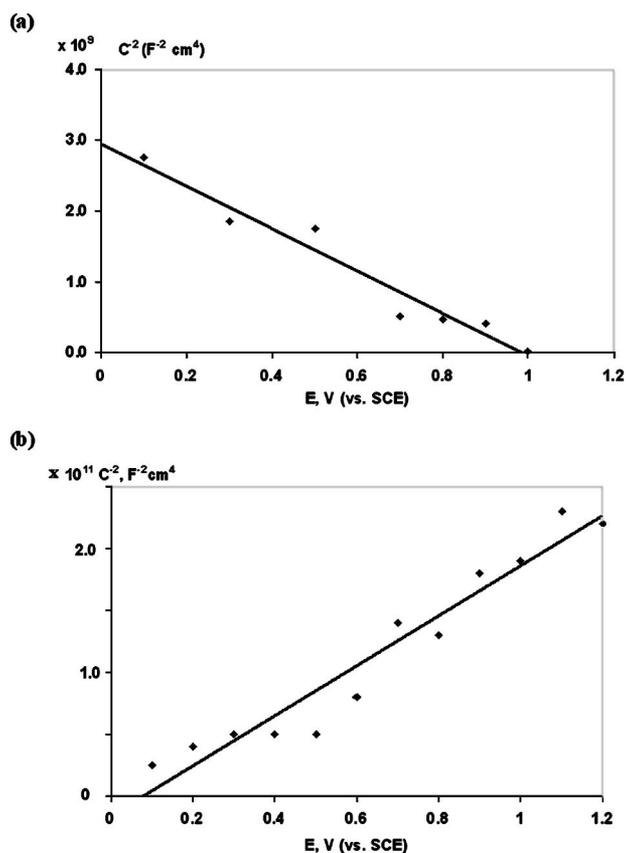


Figure 4. (a) Mott-Schottky plot, C^{-2} vs. E , from the (110) diamond film, MS1, grown in a microwave reactor. From the slope of the best straight line fit of the data, the acceptor concentration N_A , is $8.5 \times 10^{21} \text{ cm}^{-3}$. Voltage is measured vs. standard calomel electrode at room temperature. (b) Mott-Schottky plot, C^{-2} vs. E , from the (110) diamond film, MS2, grown in a microwave reactor. The average donor concentration, N_D , was calculated to be $2 \times 10^{21} \text{ cm}^{-3}$.¹⁷

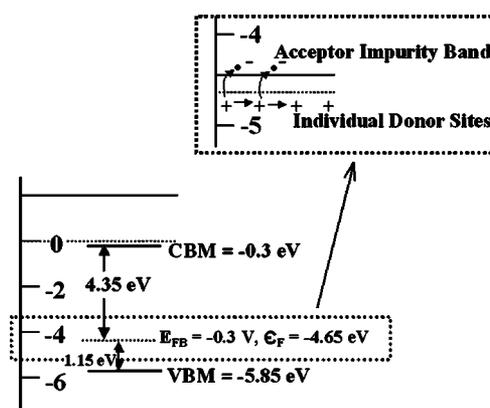


Figure 5. Schematic representation of the proposed conduction mechanism based on the presence of an acceptor impurity band within the bandgap causing n-type conductivity.²⁹

chemical measurements presented in previous publications and here strongly suggest that the co-doped samples exhibit n-type conductivity.^{17,18}

Typically, n-type conduction is achieved by activation of electrons from the donor level into the conduction band. For example, in the case of phosphorus-doped diamond the donor level is located ~ 0.6 eV below the conduction band. The present UPS analyses provide experimental support that the Fermi level is located deep within the bandgap relatively closer to the VBM and that conduction occurs by some alternate mechanism other than excitation of electrons into the conduction band.

The donor center(s) responsible for the observed n-type behavior of co-doped samples are not known. Density functional calculations by Albu *et al.*²⁹ predict that substitutional S and BS centers are deep donors, with levels at ~ 1.5 eV below the conduction band. Miyazaki and Okushi³⁰ calculated that isolated, substitutional S and the SBS complex are located 1.1-1.2 eV and 0.5 eV below the conduction band, respectively. Saada *et al.*³¹ predicted that neutral S and S^+ are located 0.15 and 0.5 eV below the conduction band, respectively. No theoretical estimates to date predict Fermi levels as deep as those indicated by the present UPS and prior Mott-Schottky results.^{17,18} These results indicate that complexes like BS and SBS are probably not responsible for the observed n-type behavior.

The observed n-type conductivity in the co-doped samples described in this work could possibly arise from the presence of an acceptor impurity band within the bandgap. If the wavefunctions of the acceptor states overlap, they may create acceptor impurity bands. Electrons from individual donor states can be excited into these acceptor bands, and hence be free to move. This model would allow conduction by electrons even if the Fermi level was low in the bandgap. Therefore, it appears that boron is not only necessary to facilitate the incorporation of sulfur into the diamond lattice, but may also contribute to the observed n-type conductivity. A schematic of this explanation is shown in Fig. 5. Some potential candidates for acceptor/donor pairs that fit this model are SVS^+/BB^- and $BSSB^+/BCH_{(i)}SB^-$.²⁹ The energy difference between these donor sites and the acceptor band would be the activation energy for conduction measured at low temperatures.

Conclusion

The band structure of homoepitaxially co-doped diamond samples was determined using both UPS and Mott-Schottky techniques. UPS results indicated that the co-doping of diamond with boron and sulfur produces surfaces exhibiting strong NEA behavior, similar to hydrogen-terminated surfaces. UPS results further showed that the Fermi level in the co-doped samples is 0.8-1.9 eV above that observed in boron-doped diamond samples. Results from Mott-Schottky plots show similar values of about 1-1.5 eV. It is hypoth-

esized that n-type conductivity stems from the excitation of electrons from donor states into an acceptor impurity band situated within the bandgap.

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