Thermionic emission from phosphorus (P) doped diamond nanocrystals supported by conical carbon nanotubes and Ultraviolet Photoelectron Spectroscopy study of P-doped diamond films.

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Abstract

Materials with low work function values (< 2 eV) are highly in demand for low temperature thermionic electron emission, which is a key phenomenon for waste heat recovery applications. Here we present the work function reduction of phosphorus (P) doped (i) diamond nano crystals grown on conical carbon nanotubes (CCNTs) and (ii) diamond films grown on silicon substrates. Thermionic emission measurements from phosphorus doped diamond crystals on CCNTs resulted in work function value of 2.23 eV. The CCNTs provide the conducting backbone for the P-doped diamond nanocrystals and the reduced work-function is interpreted as due to the presence of midband-gap state and no evidence for negative electron affinity was seen. However, Ultraviolet photo-spectroscopy studies on phosphorus doped diamond films yielded a work function value of ~ 1.8 eV with a negative electron affinity (NEA) value of 1.2 eV. Detailed band diagrams are presented to support the observed values for both cases.

1.Introduction.

Diamond with its exceptional physical and electronic properties is of great interest for scientific and technological reasons. Unique features of diamond include high carrier mobility, high thermal conductivity, high saturation velocity, high breakdown electric field, high elastic modulus, high mechanical hardness, low coefficient of thermal expansion, wide band-gap, low

coefficient of friction, and high resistance to harsh environments including radiation, chemicals, and corrosion etc. Owing to these excellent properties diamond is expected to be a promising candidate for the applications including high-power and high-frequency devices, electron emission and light emitting diodes [1]. Moreover diamond growth using chemical vapor deposition technique exhibits negative electron affinity (NEA) i.e., the presence of a vacuum level below the conduction band minimum due to hydrogen termination on the surface. This can ease the emission of electrons coming from the conduction band overcoming the small energy barrier that results from the reduced work function [2]. Experimental studies revealed that depending on orientation of diamond surface (hydrogenated by plasma) value of NEA vary from -0.7 eV to -1.3 eV [3]. In comparison to oxygen terminated diamond surfaces with value of positive electron affinity ranging from 0.54 eV to 1.7 eV and to the clean diamond surfaces with $\chi = 0.38 - 0.70$ eV [3,4]. Together with NEA and high thermal conductivity, diamond finds great potential in thermionic energy conversion of waste heat directly into electricity [2], which is the central motivation for this work.

In addition to the presence of a NEA, it was presumed that the work function of diamond could be further lowered by appropriate n type doping to bring Fermi level (E_F) closer to the conduction band minimum (CBM). We need to note that experimental study of the work function of the nitrogen doped single crystalline diamond and n type diamond films showed that situation is more complex and due to band bending at the surface reduction of the work function wasn't observed at all or was less effective than expected. Though p-type doping into diamond with boron (B) has been widely studied, it is known to introduce an acceptor level (0.37 eV) above the valance band maximum [5]. However, n-type doping into diamond is limited and has been very challenging due to lack of limited or no incorporation of dopants in to bulk diamond

lattice. Several n-type dopants such as nitrogen (N), phosphorus (P), and sulfur (S) have been studied earlier [6]. Nitrogen has been shown to create deep donor levels at 1.7 eV below the bottom of conduction band due to its structural distortion in diamond lattice. Consequently, N-doped diamond does not yield room temperature conductivity, further limiting its electronic feasibility [7]. Moreover it has been reported that the n-type conductivity of N doped polycrystalline/ultra nanocrystalline diamond (UNCD) films could be attributed to the nitrogen incorporation into grain boundaries (possibly an enhanced conductivity through interconnected shells of grain boundaries) [7]. Though theoretical modeling of sulfur (S) doping into diamond has not been reported to exhibit shallow donor levels, it is still a controversy over the type of donor level (shallow or deep) created by S [6]. Co-doping of sulfur and boron has shown to exhibit n-type conductivity, but no significant reduction in the work function has been observed [8].

Doping with phosphorus into single crystalline diamond (111) is known to create a shallow donor level 0.6 eV below the CBM [9]. It is also predicted that in P-doped diamond (polycrystalline or homoepitaxial) films at the back contact (diamond/ cathode metal), electrons can be easily extracted due to the presence of ionized donors in the space charge region [10] and due to the creation of defects during P incorporation, which in turn eases the movement of electrons to be extracted [11]. However, following factors have limited the success of controlled doping of phosphorus into the diamond lattice to any satisfactory level. First, the size of the P atom is being larger than carbon, some native defects and structural displacement will accompany during phosphorus incorporation (lattice mismatch and covalent bond length). Second, P incorporation is more favorable on (111) surface compared to (100) surface [11]. Nevertheless, considerable progress in phosphorus doped n-type diamond has been reported on

(111) and (001) orientation [9, 12-14] along with recent study on (100) oriented single crystal diamond [12] using gas phase source of phosphorus. Recently, the growth and incorporation efficiency of phosphorus as a function of surface orientation of grains in [110]-textured polycrystalline CVD diamond has been reported [15]. Growth of phosphorus doped polycrystalline diamond films on silicon substrates has also been reported using gas phase (as dopant phosphine PH_3) [16] and organic precursors in case of the single crystalline homoepitaxial P doped films grown on diamond [17]. However, thermionic emission or work function measurements have not been performed in most of these materials.

Some of the investigations based on thermionic emission from nitrogen doped homoepitaxial diamond [18], nano [19] and ultrananocrystalline diamond [20] films have resulted in observed work functions as low as 1.3 eV. In other instance, thermionic emission energy distribution (TEED) results on undoped diamond films have been shown to exhibit work function value of 3.3 eV [21]. A work function value as low as 0.9 eV has been observed for the phosphorus doped diamond film [22]. Some of the surface modifications/coatings have been reported to lower the work function values of diamond [23-28]. However, thermal stability of these surfaces has either been not tested or unsatisfactory towards the thermionic emission. Hence, the search for the proper material with required work function values is still ongoing.

Towards this goal, here we address the challenge of obtaining n-type conductivity in diamond through doping of individual diamond microcrystals which increased surface area can be expected to exhibit very interesting overall conductivity values owing to size effects. Such studies can accurately be performed using appropriate architecture that allows the synthesis of individual diamond crystals. Here, we have synthesized a new architecture consisting of diamond nanocrystals grown on the tips of conical carbon nanotube (CCNT) array [29,30] and studied the

thermionic emission properties. CCNT backbone is expected to provide conducting pathways for diamond crystals. Hence, vertically grown CCNTs allow synthesis of the diamond crystals with increased surface area as well serve as an efficient conducting channels. In addition, work function of undoped and phosphorus doped diamond films were also studied using ultraviolet photospectroscopy (UPS) for comparison.

2. Experimental.

2.1 Synthesis of the diamond crystals supported by CCNTs and diamond films on Si substrates.

CCNTs coated with diamond crystals were grown using AsTeX 5010 microwave plasma reactor (1.5 kW). The CCNT arrays synthesized on graphite foils [30,31] were used as the substrate for nucleation and growth of diamond crystals. These foil substrates were pretreated in ultrasonic diamond solution bath (0-1micron powder in acetone solution) for few seconds followed by cleaning with acetone. The foils were then immersed vertically into the plasma as shown in Figure 1(a) for the growth of diamond, similar to the growth of CCNT arrays [31] except the height of the foil substrates in this case was lowered towards the diamond growing regime inside the reactor. Di-tertiary butyl phosphine was used as the liquid source for the phosphorus doping. The schematic of the bubbler set up was shown in the Figure 1(b). Hydrogen was used as a carrier gas for the doping precursor.

Figure 1. Experimental set up for (a) growth of diamond crystals on CCNT arrays (b) bubbler set up for phosphorus doping (c) thermionic emission measurement set up.

Depositions were performed at microwave power of 900-1000W, pressures of 30-50 torr with 0.2 – 1.5% methane in hydrogen with total flow rate of 200 sccm. The phosphorus concentration was varied from 8000 – 30,000 ppm (with vapor pressure of Di-TBP being measured as 1.7 torr), varying the bubbler pressure and carrier gas (hydrogen) flow rate. Estimated phosphorous/carbon ratio during growth is 0.001– 0.004. The duration of the experiments lasted from 12 min to 1 hr. The carrier gas (H₂) flow rate of 4 - 15 sccm was used with bubbler pressure of 720 torr.

Undoped diamond films were grown on silicon wafers pretreated in ultrasonic diamond solution bath mentioned above. The growth experiments were conducted under the conditions of

3-5% methane in hydrogen (200 sccm) at 60 torr, 1450 W microwave power and the sample stage at a temperature of 650 °C for about 10 hrs. P-doping of these diamond films were performed using same dopant source as above. The conditions include 0.2 % methane in hydrogen (200 sccm) at 980 W microwave power and 50 torr pressure. The carrier gas (hydrogen) flow rate of 4 sccm is used while maintaining the bubbler pressure at 460 torr for about 9 hrs. The phosphorous concentration was 28500 ppm and estimated phosphorous/carbon ratio 0.005.

2.2 Thermionic Emission measurements.

Thermionic emission measurements were performed on each sample in a vacuum chamber with base pressure of $\sim 8 \times 10^{-8}$ Torr and 10^{-6} Torr at room temperature and 1000 °C respectively. The conducting graphite foil with synthesized CCNT's (or CCNT's with diamond) was placed on a ceramic plate (Boron Nitride) supported on a Pyrolytic BoronNitride (PBN) heater. A conducting molybdenum wire was attached mechanically to the graphite foil so that the wire and the foil act as the cathode. A molybdenum anode was arranged over the sample and attached to the micromanipulator (Figure 1(c)). The anode had a shape of the cylinder where the base is facing the sample. Diameter of the anode is 7 mm. Zero distance ($d=0$) between cathode (sample) and anode was established by observing a sudden electrical short when the anode just touched the sample. Measurements were performed at a set distance, d for different temperatures by sweeping the voltage U from 0 to 500 V while recording the current I using a pico-ammeter (Keithley 6487) equipped with a built-in variable voltage source. PBN heater was connected to a separate power supply. Temperature was measured using an infrared pyrometer (Raytek MA2SCCF; Infrared; single color; Spectral response: 1.6 μm).

2.3 Ultraviolet Photoelectron Spectroscopy.

Here, a multi chamber ultra-high vacuum (UHV) surface science facility (VG Scientific /RHK Technology) comprising of a 150 mm radius CLAM 4 hemispherical analyzer was used. The base pressure of the chamber was in the 10^{-9} torr range. A differentially pumped He-discharge lamp was used as the UV radiation source. The samples for this type of measurement typically have the active material in proper electrical contact with a gold film sputtered on copper foil to equilibrate the Fermi levels (E_F). For that reason a part of the copper foil sputtered with gold was used as the sample and the other half was used for acquiring the reference gold spectra. Double sided copper tape was used to make the electrical contact between silicon substrates with diamond films and the underlining gold film on copper foil. The measurements were performed using He-I (21.23 eV) and He-II (40.81 eV) UV excitations. A stable bias was provided to avoid the instrumental cutoff in the lens system of the analyzer at low kinetic energy (KE) for all the UPS spectra measurements. The external bias was taken into consideration in order to shift the spectra back to zero-bias position through post acquisition data processing. The calibration of the UPS spectrometer was performed by measuring the absolute position of the Fermi level of the gold sample using He-I. A spectrum, measured using a negative bias of 4.9eV is shown in the Figure 2(a) resulting in an E_F value of 21.23 eV that is in well agreement with the expected value. Similarly He-II spectrum (Figure 2(b)) shows Fermi level value of 40.83 eV, which also agrees with the literature value [32]. As the active sample is in electrical contact with the reference gold film, the sample also has the same Fermi level as of the gold. The work function of the material is then determined from the intersection of low-KE cut off tail with the background level.

Figure 2. UPS spectra of gold film showing Fermi level positions at (a) 21.23 eV for He I (b) 40.83 eV for He II radiations. Insets show magnified part of UPS spectra with Fermi edge.

3. Results and Discussion.

3.1 CCNTs coated with diamond crystals.

Figure 3 shows the SEM images of bare CCNTs, CCNTs coated with undoped diamond crystals, and CCNTs coated with P-doped diamond crystals. The size of the undoped and P-doped diamond crystals is in the range of 1-2 μm . The presence of the phosphorus in the diamond crystals was confirmed from the Secondary ion mass spectroscopy (SIMS) as shown in Figure 4, but quantitative value cannot be reported reliably owing to the rough analytical surface. Note that the very rough analytical surface results in a uniform P concentration at larger depths rather than a P tail off presumably due to the increase in roughness exposing more of the nanotubes during the profiling.

Figure 3. Scanning electron microscope (SEM) images of individual a) as synthesized CCNT b) undoped diamond coated CCNT c) P-doped diamond coated CCNT

Figure 4. Secondary ion mass spectroscopy (SIMS) depth profile of phosphorus in P-doped diamond crystals on conical carbon nanotubes. Vertical axis represents an approximate concentration.

The role of the resistivity of the substrate can be mostly ruled out, due to the presence of the conducting substrate (graphite foil) and conducting underlying structures (CCNTs) for the diamond emitters. This is advantageous for the emission applications where the resistivity of the substrate plays an important role on the values of emission currents. Even though the resistivity of the molybdenum substrate is lower compared to silicon substrate, in the present case this problem can be completely eliminated.

3.2 Thermionic Emission and work function determination.

The work function was calculated using Richard-Dushman formula [33,34]

$$J_0 = AT^2 e^{-\left(\frac{\Phi}{kT}\right)} \quad (1)$$

which describes temperature dependence of the zero field current density J_0 on the temperature T . Where Φ is the work function of given material; k is the Boltzmann constant. Constant A can be expressed by equation, $A = \lambda_B \cdot \lambda_R \cdot A_0$ [35]. Where A_0 is Richardson constant and λ_R and λ_B are material-specific correction factors. Thus the value of constant A could significantly vary from the value of Richardson constant A_0 [36].

Zero field thermionic emission current density J_0 could be calculated from the formula that describes the Schottky effect [33,34]

$$J = J_0 e^{-\left(\frac{C\sqrt{E}}{kT}\right)}$$

Where $C = \sqrt{\frac{e^3}{4\pi\epsilon_0}}$; ϵ_0 is an electric constant. E is the electric field on cathode (sample's)

surface and can be expressed by voltage drop between anode and cathode U , as $E = \alpha U$. The constant α depends on the geometry of the cathode structure [36]. Thus by rearranging and replotting thermionic I - U characteristic (Figure 5(a)) curves as $\ln(I)$ vs $\sqrt{U}$ (Figure 5(b)), the value of zero field current I_0 can be extracted for each temperature. The temperature dependence of zero field current, I_0 is plotted in Figure 5(c), which follows Richardson–Dushman model.

Hence the plot of $\ln\left(\frac{I_0}{T^2}\right)$ vs. $1/T$ should result in a straight line (Figure 5(d)) with the slope being ϕ/kT . For doped diamond supported on CCNTs a work function value of ~ 2.23 eV was obtained by this analysis.

Using the same method we obtained work function values for bare CCNTs [31] and CCNT coated with undoped diamond. I - U and $\ln(I) - U^{1/2}$ curves for bare CCNTs (Figure 6(a) and (b)) and CCNTs with undoped diamond (Figure 6(c) and (d)) are presented at varying temperatures.

Figure 5. P doped diamond crystals on CCNTs: (a) Thermionic I-V characteristics for different temperatures, (b) $\text{Ln}(I)$ vs $U^{1/2}$ (c) Richardson-Dushman curve (d) linear fit of the experimental points - $\text{Ln}\left(\frac{J_0}{T^2}\right)$ vs $\frac{1}{T}$.

Figure 6. Thermionic I-V characteristics and $\ln(I)$ vs $U^{1/2}$ plots for: (a,b) bare CCNTs [37] and (c,d) CCNT's with undoped diamond.

Figure 7 summarizes the analysis of Richardson–Dushman formalism for all three samples. The work function values obtained for bare CCNTs, undoped diamond coated CCNTs and P-doped diamond coated CCNT are 4.1 eV [31], 4.26 eV and 2.23 eV respectively. The temperature (1053 K) at which we were able to observe emission current in case of P-doped diamond is lower than for the other two samples, which could be attributed to its lower work function value.

Considering the diamond crystals at the tips being the emitting area, the experimental value of the emission constant A is $0.14 \text{ A/cm}^2\text{K}$. The maximum obtained value of current density is $575 \mu\text{A/cm}^2$ at temperature 1303 K ($1030 \text{ }^\circ\text{C}$).

Figure 7. Thermionic emission data (dots) and data-fit (line) to Richardso-Dushman equation from thermionic emitters based on bare CCNTs (red), CCNT coated with undoped diamond (green) and CCNT coated with phosphorus doped diamond (blue).

It is clearly evident that phosphorus doped diamond has significantly lower work function value compared to bare CCNT arrays and undoped diamond coated CCNT arrays. However, reported value of the work function for P doped diamond film obtained by thermionic emission method - 0.9 eV [22] is significantly lower than ours. The main reason for higher value of work function for the CCNTs coated with P doped diamond is the loss of NEA during the measurements at high temperatures. Previous studies have shown that NEA is lost in the temperature range of $700 \text{ }^\circ\text{C}$ – $900 \text{ }^\circ\text{C}$ [21, 37, 38]. Minimum temperature at which we were able to measure field enhanced thermionic emission current was about $780 \text{ }^\circ\text{C}$ for P doped diamond sample. Thus reduction of

the work function is attributed most probably only to the raising of the Fermi level closer to the conduction band from donor states of phosphorus. However in order to obtain a clearer picture, further assumptions needed to be made.

Previous studies have shown that highly P doped diamond (face (111)) has upward band bending of 3 eV toward surface [14]. The main factor causing such large value was the position of the surface E_{Fs} , found to be 1.9 eV and 1.6 eV from the valence band maximum at the surface (VBM_s) for H terminated and O terminated surfaces respectively of P doped diamond, which is lower than the bulk E_F situated 0.6 eV below CBM. Surface E_{Fs} position is determined by the characteristic surface states, which depend on the amount and nature of the surface defects. It was inferred that diamond surface defects have graphitic nature with charge neutrality point (CNP) estimated to be 1.4 eV above VBM [14,39].

Depending on the type of doping, surface Fermi level can be shifted relatively to CNP. Thus the mechanism of upward bending toward the surface for P doped diamond (in general n type) was explained qualitatively as the surface E_{Fs} shifting and pinning caused by surface defects in the form of graphitic patches or sp^2 bonded carbon atoms [14,39]. SEM images show highly defective surfaces of diamond crystals grown on CCNTs. We can apply this mechanism of band bending in our case (diamond on CCNTs and diamond film) under the assumption that the approximate position of the surface E_{Fs} for P doped diamond to be $\sim 1.8 - 2.0$ eV above VBM.

Figure 8 shows the band diagrams of diamond surface constructed in order to explain the possible scenarios according to the measured values of work functions of the diamond coated CCNTs. For that purpose, in addition to the position of the Fermi level, it is needed to know the values of the positive electron affinity (PEA) and the band bending η . It has been reported that

donor level for P in diamond is 0.6 eV below CBM in the bulk [9]. The value of PEA for clean diamond surfaces has been reported to be about 0.38-0.7 eV [3,4] for a nod doped diamond while the band gap (ΔE) is ~ 5.5 eV. Undoped polycrystalline diamond films have p type properties with the bulk E_F lying ~ 1 eV above VBM [21].

a)

CCNT's + P doped diamond

$$\begin{aligned} \text{CBM} - E_{F_s} &= 2.23 - \chi \\ 0.6 + \eta &= 2.23 - \chi \end{aligned}$$

CCNT's + undoped diamond

$$\begin{aligned} \text{CBM} - E_{F_s} &= 3.88 \text{ eV} \\ E_{F_s} - \text{VBM} &= 1.62 \text{ eV} - \eta \end{aligned}$$

b)

CCNT's + P doped diamond

$$E_F - \text{MBG} = 5.5 - (5.5 - (0.6 + \eta) + 2.23 - \chi)$$

$$E_F - \text{MBG} = \eta - \chi - 1.63 \text{ eV}$$

CCNT's + undoped diamond

$$E_F - \text{MBG} = 5.5 - (1 + \eta + 3.88)$$

$$E_F - \text{MBG} = 0.62 \text{ eV} - \eta$$

c)

CCNT's + P doped diamond

$$\text{CBM} - E_{F_s} = 2.23 - \chi$$

$$\text{CBM} - E_{F_s} + \eta = 2.23 - \chi$$

Figure 8. Surface energy band diagram of P doped and undoped diamond grown on CCNT's: a) no midband-gap states - work function value comes from position of Fermi level only; b) presence of the midband-gap state; c) only for CCNTs with P doped diamond - bulk Fermi level is much lower in the band gap and there is weak band bending. By short dashed line denoted conduction band minimum (CBM_s) and valence band maximum (VBM_s) at surface. By long dashed line denoted Fermi level and midband-gap state (MBG).

We propose three possible scenarios which result in obtained value of work function for P doped diamond grown on CCNTs stems: first is the pinning of the bulk Fermi level to the surface Fermi level and resulting in band bending. In second case could be considered combination of the pinning and the presence of the midband-gap (MBG) state originated from defects (due to doping and morphology of the individual diamond crystals) (Figure 8) [21]. Finally the third possibility (regarding only P doped diamond coated CCNTs) is that presence of the defects and impurities could cause lowering of the bulk Fermi level. As an additional effect - surface states could be compensated by the donors and defects. Based on the band diagrams we can give more detail description of possible cases for P doped diamond on CCNTs which can result in such values of work function:

(i) there is no midband-gap states (or it's overlapping with Fermi level), which results probably in lower value of upward band bending $\eta = 1.63 - \chi$ than it was reported for P doped diamond. Position of surface Fermi level E_{Fs} below conduction band minimum at the surface (CBM_s) ($CBM_s - E_{Fs} = 2.23 - \chi$) would imply low amount of surface graphitic defects;

(ii) If we assume the presence of the midband - gap states for CCNTs coated with P doped diamond crystals we can define energy difference between MBG and Fermi level at the surface which depends on the value of the band bending η

$$E_F - MBG = \Delta E - [(E_{Fs} - VBM) + (CBM - MBG)] \quad (1)$$

$$E_F - MBG = 5.5 - [(5.5 - (0.6 + \eta)) + 2.23 - \chi] = \eta - \chi - 1.63 \text{ eV}$$

and for CCNTs coated with undoped diamond

$$E_F - MBG = \Delta E - [(CBM - MBG) + (E_{Fs} - VBM)] \quad (2)$$

$$E_F - MBG = 5.5 - (3.88 + 1 + \eta) = 0.62 \text{ eV} - \eta$$

Based on the previous reports about the position of pinned Fermi level for P doped diamond - if $E_{Fs} - VBM = 1.6 \text{ eV}$; obtained value of band bending η would be $3.86 - \chi$, whereas if $E_{Fs} - VBM = 2 \text{ eV}$ then $\eta = 2.9 \text{ eV}$.

(iii) Lowering of the bulk Fermi level and raising of the surface Fermi level due to surface (state compensation) would result in weak band bending. In this situation energy difference would be expressed as follows

$$CBM - E_f = 2.23 - \chi - \eta \quad (3)$$

Considering weak band bending we can write that $\eta \rightarrow 0$ and $CBM - E_f = 2.23 - \chi$. If we assume that value of electron affinity at the surface of the doped diamond crystals would be comparable with the value of electron affinity of the clean surface of the undoped diamond – $0.38 \text{ eV} - 0.7 \text{ eV}$. We can conclude that Fermi level could be situated approximately $1.5 - 2 \text{ eV}$ below conduction band minimum.

To complete the picture of the thermionic emission mechanism from our hybrid structure we must address the fact that at lower temperatures ($< 800 \text{ }^\circ\text{C}$) we have not observed

sufficiently high values of I_{FETE} (to be detected) which is the onset of the presence of NEA. We believe that main reason is the development of the potential barrier at the CCNTs and P doped diamond interface due to band bending as shown in Figure 9 in analogous to the case of metal/n-type semiconductor structures. Considering the CCNTs as the conducting channels for diamond it is needed to attain higher temperatures (>800 °C) to obtain sufficient values of current across the interface to supply electrons for emission.

Figure 9. Schematic view of band diagram illustrating the band bending at the interface of CCNTs and diamond.

3.3 UPS and work function determination of the diamond films.

It was demonstrated that UPS measurements of diamond could provide information about electron affinity and surface Fermi level position [40]. In view of the fact that we didn't observe any evidence for NEA in case of CCNTs coated with diamond we turned our attention to P

doped diamond films grown on silicon substrate. Figure 10 shows the low kinetic energy part of the He-I emission spectra of (a) undoped and (b) phosphorous doped films. Both undoped and P-doped diamond films exhibit two peaks one for a low KE cut-off and a second high intensity peak characteristic of work function and NEA behavior with electrons coming from CBM_s respectively [40]. All the numbers for the cut off energy positions are obtained with the extrapolation to zero intensity. In the case of undoped diamond, the value of the effective work function is given as 3.9 eV and sharp peak is related to electrons thermalized to the bottom of conduction band and lower edge of sharp peak defines CBM_s position to be 4.4 eV above surface Fermi level (CBM_s – E_{FS} = 4.4 eV). The lower energy edge of the second wider peak 5.1 eV could be related to midband-gap state (CBM_s - MBG) which will be discussed further. For P-doped diamond, a low KE cut-off is situated at 1.8 eV and CBM_s position at surface situated at 3 eV giving rise to same NEA value of 1.2 eV. A work

Figure 10. Low kinetic-energy part of He – I (21.23 eV) spectra of a) undoped diamond film; b) phosphorus doped diamond film. Spectra of the undoped diamond film show low kinetic cut-off energy positions indicative of effective work function, sharp peak related to thermalized electron states and a high intensity cut-off position of conduction band minimum due to the presence of

NEA and MBG state. Spectra of the p doped diamond film has no thermalized electrons sharp peak but has visible KE cut-off of eff. work function and NEA high intensity cut-off.

function value of 4.67 eV obtained for gold film lies in the value range reported in the literature [32]. Interestingly work function value of 3.6 eV has been reported for hydrogen terminated phosphorus doped (111) single crystal diamond [14]. An upward band bending of 3.2 eV from the simulated surface Fermi level position and absence of NEA from the Secondary Electron Spectra was attributed to the large work function value. Though the presence of the NEA was predicted theoretically, the reason for the absence could not be evidently articulated [13]. The similar explanation for the lack of NEA peaks in UPS spectrum (band bending towards surface) has been proposed for N-doped diamond with H terminated surface [40]. However, in the present case the presence of NEA value of 1.2 eV evident from the UPS spectra could be attributed to the reduced work function value detected.

a)

P doped diamond film on Si/SiO₂

$$E_F - MBG = 5.5 - (5.5 - (0.6 + \eta) + 3)$$

$$E_F - MBG = \eta - 2.4 \text{ eV}$$

Undoped diamond film on Si/SiO₂

$$E_{Fs} - MBG = 1 + \eta - (5.5 - 5.1)$$

$$E_{Fs} - MBG = \eta - 0.6 \text{ eV}$$

b)

P doped diamond film on Si/SiO₂

c)

P doped diamond film on Si/SiO₂

Figure 11. Surface energy band diagrams for P doped and undoped diamond films grown on Si/SiO₂ – based on UPS results: a) presence of the midband-gap state for P doped and undoped diamond films; b) no midband-gap state for P doped diamond film; c) no midband-gap states, lowering of the bulk Fermi level and weak band bending. Energy difference for undoped diamond was obtained from equation $E_F - \text{MBG} = (E_F - \text{VBM}) - [\Delta E - (\text{CBM} - \text{MBG})]$. Dotted line in both band diagrams is the vacuum level in case of NEA. Underlined values of energies are obtained from UPS measurements. By short dashed line denoted conduction band minimum (CBM_s) and valence band maximum (VBM_s) at surface. By long dashed line denoted Fermi level and midband-gap state (MBG).

We consider three most probable scenarios for the P doped diamond films and one for the undoped diamond film which are all illustrated in the band diagram (Figure 11) constructed based on the UPS results:

(i) if there is present midband-gap state (Figure 11 a)), the energy difference between MBG and surface Fermi level for P doped diamond film and undoped diamond film respectively would be $\eta - 2.4\text{eV}$ and $\eta - 0.6\text{ eV}$. In agreement with previous assumption, if Fermi level is at $\sim 2\text{ eV}$

above VBM, in result $\eta - 2.4 \text{ eV} = 0.5 \text{ eV}$ and value of η in this case is 2.9 eV which is close to the value 3.2 eV reported by Kono et al. [14]. As for the undoped diamond films, from the band diagram we can determine the position of the surface Fermi level at 1.1 eV above VBM. From the equation describing energy difference we know that $E_{Fs} - MBG = 0.7 \text{ eV}$ and MBG position is 0.4 eV above VBM.

(ii) Upward band bending at the surface and NEA (no midband-gap states) (Figure 11 b)). Value of work function is 1.8 eV, energy difference at surface $CBM_s - E_{Fs} = 3 \text{ eV}$. Obtained upward band bending value is 2.4 eV. Thus higher than for P doped crystals on CCNTs. For undoped diamond film value of the upward band bending is ~0.6 eV where work function value is 3.9 eV and energy difference $CBM_s - E_{Fs} = 5.1 \text{ eV}$.

(iii) In the third scenario we could again assume that bulk Fermi level is significantly lower and surface Fermi level is higher in the band gap. In consequence there is no or very weak band bending. Based on UPS data Fermi level in this case would be 3 eV below CBM thus indicating the p type property of the diamond film in the bulk. We did performed thermionic emission measurements from P doped nanocrystalline diamond film (with hydrogenated surface) grown on W foil (Appendix A, Figure 12) and found that the value of effective work function is 1.33 eV. Considering the presence of NEA in case of the diamond film grown on W foil it could imply that value obtained value 1.33 eV is the difference between the surface Fermi level and CBM_s . Which would support argument about the lower position of the bulk Fermi level.

This is the first report on the work function of phosphorus doped diamond polycrystalline films, and further theoretical calculations are needed to accommodate for all the differences in the

present scenarios for the determination of position of the surface Fermi level and band bending values.

4. Conclusions.

In conclusion here we present the work function reduction of phosphorus doped (i) diamond nano crystals grown on conical carbon nanotubes (CCNTs) and (ii) diamond films grown on silicon substrates. The CCNTs provide the conducting backbone for the P-doped diamond microcrystals as well allow to increase the surface area of the former. Thermionic emission measurements from phosphorus doped diamond crystals on CCNTs resulted in work function value of 2.23 eV. The presence of hybrid structure with combination of diamond, CCNTs and graphite, prevented the determination of accurate work function of diamond by UPS. The Ultraviolet Photoelectron spectroscopy Studies on phosphorus doped diamond films yielded a work function value of 1.8 eV with observed NEA value of 1.2 eV. The origin of the reduced values of work functions is discussed using detailed band diagrams. Proposed explanation of work function reduction for the doped diamond crystals supported on CCNTs is upward band bending due to P doping and difference between bulk and surface Fermi levels. We suggest that midband-gap state due to the structural defects of the polycrystalline diamond could be an additional factor affecting value of the work function. Finally as a third possibility only for P doped diamond coated CCNTs and P doped diamond films, it could be considered significantly lower position of Fermi level than expected for this type of doping. For P doped diamond films the further decrease of work function value is attributed to negative electron affinity.

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Appendix A

Thermionic emission from P doped nanocrystalline film grown on W foil.

P doped diamond films were synthesized on W foils pretreated in ultrasonic diamond solution bath. Growth was performed under the conditions of 1.5% CH₄/H₂ at pressure 70 torr, microwave power 1000 W and temperature of the sample stage ~450°C for 2.5 hours. P doping was performed using the precursor Di-tertiary-butylphosphine. Phosphorous concentration was 6000 – 8000 ppm and estimated phosphorous/carbon ratio during growth is 0.002 – 0.003.

Thermionic emission measurements from P diamond film sample were performed following the same procedure as for the CCNTs coated with diamond. The value of the work function obtained for the P doped diamond film grown on W foil is ~1.33 eV.

Figure 12. Thermionic emission measurements from P doped film grown on W foil: a) thermionic I-V characteristic for different temperatures; b) linear fit of the experimental points - $\ln\left(\frac{J_0}{T^2}\right)$ vs $\frac{1}{T}$.

References:

- [1] Field, J. E. *The properties of diamond*. Academic Press: 1979.
- [2] Smith, J. R.; Bilbro, G. L. and Nemanich, R. J., Theory of space charge limited regime of thermionic energy converter with negative electron affinity emitter, J. Vac. Sci. Technol. B 2 (2009) 1132.
- [3] F. Maier, J. Ristein, and L. Ley, Electron affinity of plasma-hydrogenated and chemically oxidized diamond (100) surfaces, Phys. Rev. B 64 (2001) 165411.
- [4] J. B. Cui, J. Ristein, and L. Ley, Electron Affinity of the Bare and Hydrogen Covered Single Crystal Diamond (111) Surface, Phys. Rev. Lett. 81 (1998) 429; L. Diederich, P. Aebi, O. M. Kuttel, and L. Schlapbach, NEA peak of the differently terminated and

- oriented diamond surfaces, Surf. Sci. 424 (1999) L314; P. K. Baumann and R. J. Nemanich, Characterization of copper-diamond (100), (111), and (110) interfaces: Electron affinity and Schottky barrier, Phys. Rev. B 58 (1998) 1643; Y.M. Wang, K.W. Wong, S.T. Lee, M. Nishitani-Gamo, I. Sakaguchi, K.P. Loh, and T. Ando, Recent studies on diamond surfaces, Diamond Relat. Mater. **9** (2000) 1582.
- [5] Kraft, A., Doped Diamond: A Compact Review on a New, Versatile Electrode Material, Int. J. Electrochem. Sci. 2 (5) (2007) 355-385.
- [6] Mainwood, A., Theoretical modelling of dopants in diamond, J. Mater. Sci.-Mater. Electron. 17(6) (2006) 453-458.
- [7] Farrer, R. G., On the substitutional nitrogen donor in diamond, Solid State Communications 7(9) (1969) 685-688; P. Zapol, M. Sternberg, L. A. Curtiss, T. Frauenheim, D. M. Gruen, Tight-binding molecular-dynamics simulation of impurities in ultrananocrystalline diamond grain boundaries, Phys. Rev. B 65 (2001) 045403.
- [8] Eaton, S. C.; Anderson, A. B.; Angus, J. C.; Evstefeeva, Y. E.; Pleskov, Y. V., Co-doping of Diamond with Boron and Sulfur, Electrochem. Solid State Lett 5(8) (2002) G65-G68.
- [9] Hasegawa, M.; Teraji, T.; Koizumi, S., Lattice location of phosphorus in *n*-type homoepitaxial diamond films grown by chemical-vapor deposition, Appl. Phys. Lett. 79(19) (2001) 3068 -3070.
- Pinault, M.-A.; Barjon, J.; Kociniowski, T.; Jomard, F.; Chevallier, J., The *n*-type doping of diamond: Present status and pending questions, Physica B 401-402 (2007) 51-56.
- [10] Kuriyama, K.; Kimura, C.; Koizumi, S.; Kamo, M.; Sugino, T., Elucidation of field emission characteristics of phosphorous-doped diamond films, J. Vac. Sci. Technol. B 17(2) (1999) 723-727.

- [11] C Chen, C. F.; Tsai, C. L.; Lin, C. L., Electronic properties of phosphorus-doped triode-type diamond field emission arrays, *Mater. Chem. Phys.* 72(2) (2001) 210-213.
- [12] H. Kato, S. Yamasaki, H. Okushi, n-type conductivity of phosphorus-doped homoepitaxial single crystal diamond on (001) substrate, *Diamond and Related Materials* 14(11-12) (2005) 2007-2010.
- [13] Takeuchi, D.; Kato, H.; Ri, G. S.; Yamada, T.; Vinod, P. R.; Hwang, D.; Nebel, C. E.; Okushi, H.; Yamasaki, S., Direct observation of negative electron affinity in hydrogen-terminated diamond surfaces, *Appl. Phys. Lett.* 86 (2005) 152103.
- [14] Kono, S.; Mimochi, K.; Takyō, G.; Goto, T.; Abukawa, T.; Aoyama, T., Energy band diagram of a H-terminated P-doped n-type diamond (111) surface, *New Diam. Front. Carbon Technol.* 17(5) (2007) 231-242.
- [15] Lazea, A.; Barjon, J.; D'Haen, J.; Mortet, V.; D'Olieslaeger, M.; and Haenen, K., Phosphorus incorporation in plasma deposited diamond films, *J. Appl. Phys.*, 105 (2009) 083545.
- [16] Ghodbane, S.; Omnes, F.; Bustarret, E.; Tavares, C.; Jomard, F., n-type phosphorus-doped polycrystalline diamond on silicon substrates, *Diamond and Related Materials* 17 (7-10) (2008) 1324-1329.
- [17] Kato, H.; Yamasaki, S. and Okushi, H., Growth and characterization of phosphorus-doped diamond using organophosphorus gases, *Phys. Stat. Sol. A - Applications and Materials Science* 202 (11) (2005) 2122-2128.
- [18] Kataoka, M.; Zhu, C. Y.; Koeck, F. A. M.; Nemanich, R. J., Thermionic electron emission from nitrogen-doped homoepitaxial diamond, *Diamond and Related Materials* 19 (2-3) (2010) 110-113.

- [19] Suzuki, M.; Ono, T.; Sakuma, N.; Sakai, T., Low-temperature thermionic emission from nitrogen-doped nanocrystalline diamond films on n-type Si grown by MPCVD, *Diamond and Related Materials* 18 (10) (2009) 1274-1277.
- [20] Koeck, F. A. M.; Nemanich, R. J., Low temperature onset for thermionic emitters based on nitrogen incorporated UNCD films, *Diamond and Related Materials* 18 (2-3) (2009) 232-234.
- [21] Uppireddi, K.; Westover, T. L.; Fisher, T. S.; Weiner, B. R.; Morell, G., Thermionic emission energy distribution from nanocrystalline diamond films for direct thermal-electrical energy conversion applications, *J. Appl. Phys.* 106 (2009) 043716.
- [22] Koeck, F. A. M.; Nemanich, R. J.; Lazea, A.; Haenen, K., Thermionic electron emission from low work-function phosphorus doped diamond films, *Diamond and Related Materials* 18 (5 - 8) (2009) 789-791.
- [23] Nemanich, R. J.; Bergman, L.; Turner, K. F.; Vanderweide, J.; Humphreys, T. P., Properties of interfaces of diamond, *Physica B* 185 (1-4) (1993) 528-538.
- [24] Benndorf, C.; Hadenfeldt, S.; Luithardt, W.; Zhukov, A., Photoelectron spectroscopic investigations and exoelectron emission of CVD diamond surfaces modified with oxygen and potassium, *Diamond and Related Materials*, 5 (6-8) (1996) 784-789.
- [25] Vanderweide, J.; Nemanich, R. J., Influence of interfacial hydrogen and oxygen on the Schottky barrier height of nickel on (111) and (100) diamond surfaces, *Phys. Rev. B* 49 (19) (1994) 13629-13637.
- [26] Geis, M. W.; Twichell, J. C.; Macaulay, J.; Okano, K., Electron field emission from diamond and other carbon materials after H₂, O₂, and Cs treatment, *Appl. Phys. Lett.* 67(9) (1995) 1328-1330.

- [27] Wong, K. W.; Wang, Y. M.; Lee, S. T.; Kwok, R. W. M., Negative electron affinity on polycrystalline diamond surface induced by lithium fluoride deposition, *Diamond and Related Materials* 8 (10) (1999) 1885-1890.
- [28] Wong, K. W.; Wang, Y. M.; Lee, S. T.; Kwok, R. W. M., Lowering of work function induced by deposition of ultra-thin rubidium fluoride layer on polycrystalline diamond surface, *Appl. Surf. Sci.* 140 (1-2) (1999) 144-149.
- [29] Dumpala, S.; Jasinski, J. B.; Sumanasekera, G. U.; Sunkara, M. K., Synthesis of Conical Carbon Nanotube Arrays: Mechanistic Aspects and Growth on Foil Substrates, *Carbon* 49 (2011) 2725 –2734.
- [30] Sherehiy, A.; Dumpala, S.; Safir, A.; Mudd, D.; Arnold, I.; Cohn, R. W.; Sunkara, M. K. Sumanasekera, G. U., Thermionic emission properties and the work function determination of arrays of conical carbon nanotubes, *Diamond and Related Materials* 34 (2013) 1–8.
- [31] Chernomordik, B.; Dumpala, S.; Chen, Z.Q.; Sunkara, M.K., Nanodiamond Tipped and Coated Conical Carbon Tubular Structures, *Chem. Vap. Depos.* 14 (2008) 256-262.
- [32] Rentenberger, S.; Vollmer, A.; Zojer, E.; Schennach, R.; Koch, N., UV/ozone treated Au for air-stable, low hole injection barrier electrodes in organic electronics, *J. Appl. Phys.* 100 (5) (2006) 053701.
- [33] Reimann, A. L. *Thermionic Emission*; John Wiley and Sons, Inc.: New York, 1934; Chapter 1, p 61.
- [34] Modinos, A. *Field, Thermionic, and Secondary Electron Emission Spectroscopy*; Plenum Press: New York, 1984; Chapter 1, pp 20-22.

- [35] Koeck, F. A. M.; Nemanich, R. J., Emission characterization from nitrogen-doped diamond with respect to energy conversion, *Diamond & Related Materials* (15) (2006) 217 – 220.
- [36] Liu, P.; Sun, Q.; Zhu, F.; Liu, K.; Jiang, K.; Liu, L.; Li, Q.; Fan, S., Measuring the Work Function of Carbon Nanotubes with Thermionic Method, *Nano Leterrs* 8 (2) (2008) 647–651.
- [37] Köck, F. A. M.; Garguilo, J. M.; Brown, B. and Nemanich, R. J., Enhanced low-temperature thermionic field emission from surface-treated N-doped diamond films, *Diamond and Related. Materials.* 11 (2002) 774.
- [38] Koeck, F. A. M.; Garguilo, J. M. and Nemanich, R. J., On the thermionic emission from nitrogen-doped diamond films with respect to energy conversion, *Diamond and Related Materials* 13 (2004) 2052.
- [39] Ristein, J.; Maier, F.; Riedel, M.; Cui, J.B. and Ley, L., Surface Electronic Properties of Diamond, *Phys. Stat. Sol. (a)* 181 (2000) 65.
- [40] Diederich, L.; Kuttel, O. M.; Ruffieux, P.; Pillo, T.; Aebi, P.; Schlapbach, L., Photoelectron emission from nitrogen- and boron-doped diamond (100) surfaces, *Surf. Sci.* 417 (1998) 41-52.