Low-voltage ionization of air with carbon-based materials

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Abstract
Polycrystalline diamond and carbon nanotubes (CNTs) exhibit excellent vacuum field emission properties, characterized by low turn-on voltage and high current density. Their atmospheric field emission and ionization capabilities are reported in this paper. Highly graphitic polycrystalline diamond (HGPD) film was grown in a plasma-enhanced chemical vapour deposition process, and its ability to ionize atmospheric air was characterized and compared against CNTs. The HGPD sample was activated by applying a moderate voltage bias (340 V) for an extended period across a 10 µm electrode gap. After activation, a turn-on voltage of 20 V and a sustainable current of 10 µA were observed with the same gap. Results also indicate that field emission helps to create a moderate ionization effect without catastrophic air breakdown. A hydrogen plasma treatment is shown to restore emission current back to or even exceeding the original level, which suggests an important role of surface termination in the electron emission process. CNTs were grown and tested but did not perform as well under similar conditions.

1. Introduction
The negative electron affinity (NEA) [1] and grain-boundary geometric field enhancement of polycrystalline diamond make this material an ideal low-voltage electron field emission source. In addition to its excellent field emission properties, the integrity and longevity of diamond are beneficial for practical devices operating either under vacuum or at atmospheric pressure. Particularly in ion generation devices, ion bombardment of the cathode surface requires the cathode material to possess superior mechanical strength and chemical inertness. Traditional ion generation devices suffer from inherent difficulties of operation at high voltages; therefore, they are very difficult to integrate into low-voltage microscale ion-generation devices, which have potential applications in microscale mass spectroscopy [2], ion mobility spectroscopy [3] and microscale electronics cooling devices [4].

In addition to polycrystalline diamond, carbon nanotubes (CNTs) exhibit excellent potential as low-voltage cold electron sources [5]. CNTs can enhance macroscopic electric fields by several orders of magnitude as a result of their high aspect ratios. Zhao and Buldum [6] used density functional theory (DFT) to show that field emission from CNTs is enhanced by the absorption of various gas molecules (O₂, N₂, etc.), suggesting an ion generation device utilizing CNTs. One concern when utilizing CNTs for producing ions is their long-term robustness as field emitters. Bonard et al [7] reviewed CNT degradation mechanisms and showed that degradation is often caused by mechanical failure of the contact at low applied fields and by resistive heating (probably exacerbated by mechanical stress) at high emission currents. This paper describes the synthesis and performance of highly graphitic polycrystalline diamond (HGPD) films and CNTs used as low-voltage atmospheric ionization sources.

The key processes in vacuum field emission from diamond are the injection of electrons into the conduction band and the transport of electrons to the surface from which they are emitted into vacuum by quantum tunnelling [8]. However, the detailed emission mechanism of NEA diamond films is not as well understood as that of other carbon-based materials such as CNTs [9]. Desirable features in a diamond field emitter typically include low resistivity, high defect density and high grain boundary density [10]. These desired properties can be achieved by depositing diamond films with

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high graphitic content (making the film conducting), doping (introducing inter-band energy levels and adding defects) and nanocrystalline forms of diamond (increasing grain boundary density).

In atmospheric environments, field-emitted electrons collide with neutral air molecules and ionize them with some probability. The impact ionization probability is determined by the electron energy and the associated electron–molecule cross-sections. A released electron can also ionize air molecules once its kinetic energy exceeds a threshold (∼15 eV in air), resulting in an avalanche process. The number of ionizing collisions undergone by an electron per unit length in the direction of an electric field is referred to as Townsend’s first ionization coefficient, α [11]. The combined field emission and air ionization process can produce a self-sustained current flow (ranging from picoamperes to microamperes) between an anode and a cathode without catastrophic breakdown. 

Zhang et al [12] simulated the dominant collision reactions with a direct simulation Monte Carlo technique and predicted ion generation rates in atmospheric air due to field-emitted electrons. Their results indicated that understanding the role of field-emitted electrons is pivotal to the study of ionization in small electrode spacings ranging from 1 to 10 μm.

Paschen [13] studied the relationship between the breakdown voltage of a gas and the product of pressure, p, and gap separation, d. The resulting Paschen’s curve represents breakdown voltage as a function of pd. At very low and very high values of pd, deviations from Paschen’s curve become evident, and Paschen’s curve is no longer valid. The breakdown curve in microscale gaps has been investigated more recently by Torres and Dhariwal [14], who reported significant deviations from Paschen’s curve at gap separations between 0.5 and 25 μm for several different cathode materials. Dhariwal et al [15] later provided an explanation for the deviation based on tunnelling of electrons in a study of micro-motors and micro-actuators. Lee et al [16] observed results similar to those of Torres and Dhariwal while investigating electrode erosion caused by arc discharges. Slade and Taylor [17] compared the work of Dhariwal et al and Lee et al., and applied a linear-fit equation to the breakdown voltage versus gap spacing data. They also introduced the effect of cathode micro-projections into the Fowler–Nordheim equation to quantify the role of field emission as an electron source in the breakdown process. Although the cited prior work on microscale ionization has produced some useful physical insights, ionization processes in microscale gaps with high-performance field-emission cathodes have not been tested and documented to date.

To investigate the generation of ions in air, it is necessary to understand both field emission and subsequent electron–air molecule impact ionization processes. Most prior work has focussed on electron emission in vacuum; however, more recent studies have suggested that the presence of environmental gases can enhance field emission [18–23]. Field emission from polycrystalline diamond exhibits significantly higher emission current density and lower turn-on fields when compared with, for example, tungsten emitters. Diamond is also well known as the hardest chemically-inert material, and thus is expected to survive ion bombardment. Nanoscale structures made of polycrystalline diamond can be fabricated and used to enhance macroscopic electric fields. Kang et al [24] fabricated moulded polycrystalline diamond tips using conventional silicon micro-fabrication methods in conjunction with diamond deposited by plasma-enhanced chemical vapour deposition. They achieved a radius of curvature at the tip of the samples between 5 and 10 nm. The small radius of curvature increases the local electric field at the tip by geometrically enhancing the applied macroscopic electric field. CNTs also enhance macroscopic electric fields due to their high aspect ratios, but their applicability and long-term reliability for ionization of air remains questionable. As air molecules are ionized, positive ions impact the cathode surface at relatively high energies, typically forcing an electron to be released from the cathode surface. This process can degrade the performance of the emitting surface over a period of time. HGPD and CNTs emitters are grown and compared as low-voltage atmospheric ion generators in this work. The overall objective of this paper is to investigate the possibility of enhanced emission and ionization characteristics of carbon-based cathodes in atmospheric air.

### 2. Sample preparation and experimental set-up

CGT and HGPD sample synthesis occurred in a SEKI AX5200s microwave plasma-enhanced chemical vapour deposition reactor. Synthesis parameters for CNT and HGPD samples, such as substrate voltage bias (dc), microwave plasma power, chamber pressure and process gas (H₂ and CH₄) flow rates, are listed in table 1. For HGPD, a diamond-powder-scratched tungsten substrate was prepared, and for CNTs, a 20 nm aluminium and a 4 nm iron catalyst layer were thermally evaporated on a silicon substrate.

For the HGPD film, the pre-polished tungsten substrate was placed on a 5.10 cm diameter molybdenum puck and inserted into the reactor chamber. The puck served to concentrate plasma directly above the sample. The chamber was slowly evacuated to a pressure of 133.3 Pa (1 Torr) by an external mechanical pump. Hydrogen (Praxair 4.5 grade) gas was then introduced into the chamber maintained at approximately 799.9 Pa (6 Torr) for 10 min at a flow rate of 50 sccm (standard cubic centimetres per minute) to purge the chamber. The chamber was then pressurized with hydrogen gas to 5333 Pa (40 Torr) at a flow rate of 200 sccm. Induction substrate heating was applied by a 3.5 kW RF source acting on a graphite susceptor upon which the molybdenum puck rested. A K-type thermocouple embedded in the centre of the susceptor and located at a depth of 2.54 mm from the top of the susceptor surface allowed feedback control. The

| Table 1. PECVD synthesis parameters for HGPD and CNT. |
|----------------|-------------|-------------|
| Synthesis parameters | HGPD | CNT |
| Pressure (Pa) | 5333 | 1333 |
| Stage temperature (°C) | 630 | 710 |
| Plasma power (W) | 1000 | 150 |
| Bias (V) | −200 in nucleation step, 0 in growth step | 9/45 |
| CH₄/H₂ flow rate (sccm) | 8/200 in nucleation step, 4/200 in growth step | |
| Time | 1 h in nucleation step, 12 h in growth step | 15 min |
temperature of the substrate’s top surface was measured by a Williamson (model 90) dual wavelength pyrometer focused on top of the substrate. After the susceptor temperature stabilized at 630 °C (the pyrometer reads 770 °C for the sample surface temperature), a hydrogen plasma was initiated at a power of 1000 W. The plasma was maintained by a 2.45 GHz microwave generator (ASTeX AX2100). A −200 V bias was applied to the substrate, followed by initial methane (Praxair ultra high purity) introduction at a flow rate of 8 sccm, beginning the 1 h nucleation process. At the end of the nucleation process, substrate bias was reduced to −100 V, and the methane flow rate was reduced to 4 sccm to begin the 12 h growth process for the diamond film. After terminating diamond synthesis, the reactor was evacuated, and the sample was allowed to cool to room temperature. Nitrogen gas (Praxair 4.8 grade) was then introduced to pressurize the chamber, and the sample was removed. CNT growth was performed in the same manner with different synthesis parameters in which growth typically lasted 15–30 min without the nucleation step and with a plasma power of 150 W.

After growth of each sample, scanning electron microscope (SEM) images were recorded. A continuous HGPD film can be observed in figure 1(a) with a grain size of approximately 1 μm. Figure 1(b) shows the edge of the HGPD film and the exposed tungsten substrate. The thickness of HGPD film is estimated to be approximately 3 μm. Figure 2 shows the mat-type, highly-packed and multi-walled CNT array sample with approximately 40 nm diameters and 1 μm length, typical of CNTs synthesized by PECVD [25]. A Raman spectrum of HGPD was recorded and is shown in figure 3. The peak at 1335 cm⁻¹ is a clear indication of diamond (sp³) bonding while the peak at 1580 cm⁻¹ reveals the substantial presence of graphitic (sp²) carbon content in the sample.

The major elements of the point-to-plane two-terminal apparatus, shown in figure 4, are two electrodes: an anode and a cathode. The anode refers to the positively biased electrode, whereas the cathode refers to the negatively biased electrode. Most experiments were conducted in the forward bias mode with the emitter sample as the cathode and a silver rod as the anode while some samples were tested under reverse bias. Air was ionized by physically separating the anode and cathode by a controlled distance and then applying a voltage bias between the electrodes. Typical operating voltages were of the order of several hundreds of volts, and the measured currents ranged from fractions of picoamperes to tens of microamperes. Current measurements were obtained from a Keithley 6485 picoammeter via an IEEE-488 (GPIB) bus
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Figure 3. Raman spectrum of the HGPD sample.

Figure 4. Schematic diagram of the two-terminal point-to-plane apparatus in the forward bias setup.

connected to a PCI-GPIB controller installed on a personal computer. Current–voltage results presented in this paper represent the average current from 200 data samples per applied voltage that were recorded over an 11.5 s period with a 0.058 s interval between readings. Voltage measurements were obtained from a KEPCO BHK power supply and represent the local voltage at the output terminals. An inchworm motor, which utilizes piezoelectric actuators attached to a linear translation stage with crossed-roller bearings, was used to control the spacing between the anode and cathode. An optical position encoder and feedback loop were incorporated into the inchworm motor to provide 0.5 μm spatial resolution. The 75 mm × 75 mm translational stage was mounted directly onto an optical tabletop. A micromanipulator was also attached to the translation stage and it held the 3 mm diameter silver rod anode. The sample was sandwiched between a 7.0 mm thick Plexiglas plate with approximately 25 mm diameter through-holes to accommodate various sized samples and a molybdenum electrical contact plate, which was placed on top of a 6.0 mm thick plate of glass (as shown in figure 4). A Plexiglas container enclosed this entire apparatus to prevent dust and any room draughts from affecting the experiment.

Figure 5. Current as a function of time showing initial activation of an HGPD sample in the first long-term test. Applied bias = 340 V. Test period = 12 h.

Figure 6. Current as a function of voltage plot after first activation process. The inset highlights the low bias range. ■: ramp-up under forward bias; ▲: ramp-down under forward bias.

3. Results and discussion

The HGPD sample was tested on the two-terminal apparatus described in the previous section. In the first test, a current of 10 nA was measured at 300 V forward bias with a 10 μm gap separation. The voltage was then increased to 340 V and held constant for approximately 12 h. Application of the constant voltage for an extended period of time produced improved emission results [26]. Current as a function of time in the initial 12 h activation process is shown in figure 5. The initial current of tens of nanoamperes increases sporadically and finally increases to several microamperes. After the activation process, current–voltage tests were performed and the results are shown in figure 6. The inset of figure 6 shows the low current range. It can be seen that the sample turned on at approximately 20 V after the initial activation process. The turn-on voltage is defined as the voltage needed to maintain a 5 pA current, which is measurably larger than our average circuit noise level. Above-turn-on voltages generated several microamperes of current subsequently. A maximum current of 10.4 μA was recorded at 340 V, which was the maximum voltage applied during this test.
The current as a function of time for the second long-term test is shown in Figure 7. Applied bias = 340 V. Test period = 40 h.

The inset of Figure 8 shows that the sample turned on at approximately 20 V for both gap separations. The inset of Figure 8 shows that the sample turned on at approximately 20 V for both gap separations. The inset of Figure 8 shows that the sample turned on at approximately 20 V for both gap separations.

Figure 7. Current as a function of time for the second long-term test. Applied bias = 340 V. Test period = 40 h.

Figure 8. Current as a function of voltage during ramp-up under forward bias after the second long-term test for 10 (■) and 20 µm (▲) gaps. The inset highlights the low bias range.

The same location on the sample was then tested at 340 V for long-term reliability and resulted in a second activation process. Figure 7 shows a current versus time plot over a 40 h time period. Significant current fluctuation in the first 15 h is observed. After the first 15 h, the current increased rapidly and remained relatively stable at approximately 10 µA for 25 h. Current–voltage tests were performed again after the 40 h activation test (see Figure 8). The inset of Figure 8 shows that the sample turned on at approximately 20 V for both gap separations. The inset of Figure 8 shows that the sample turned on at approximately 20 V for both gap separations. The inset of Figure 8 shows that the sample turned on at approximately 20 V for both gap separations.

After activating a second spot on the sample for several hours at 240 V, several current–voltage tests were performed at a series of different gap separations (2, 3, 4, 5, 6, 8, 10 and 12 µm), and turn-on voltages are shown in Figure 9 compared with the traditional Paschen’s curve for an iron cathode surface [27] and the electrical breakdown voltage curve reported by Lee et al [16]. The turn-on fields for the respective gap separations were as follows: 35, 33, 30, 32, 28, 25, 21 and 22.5 V µm⁻¹, which are significantly larger than the results on the first spot, indicating the non-uniformity of the HGPD film. The turn-on field generally decreases as the gap increases because more ionization events occur and release free electrons inside the gap, thus generating larger currents as the gap increases. For very small gaps (significantly less than the mean free path of electrons in air), negligible numbers of molecules are ionized along the nearly ballistic electron path, and the current measured is primarily caused by field emission alone. Between gaps of 2 and 12 µm, the current likely derives from a combination of ions and electrons produced by impact ionization and field emission. As the gap becomes larger, the voltage needed to create the same magnitude of electric field must increase and it quickly approaches the breakdown voltage, meaning that catastrophic breakdown would occur before significant field emission is initiated. Therefore, the region between the electrical breakdown voltage curve [16] and the turn-on voltage curve in Figure 9 is the working area for microscale field-emission ionization devices.

Figure 9. Comparison between traditional Paschen’s curve on an iron cathode surface [27], the electrical breakdown voltage curve for microscale gaps reported by Lee et al [16], and the turn-on voltage curve measured in this work.

After several days of testing, the emission current from the sample degraded to a few nanoamperes at 300 V applied voltage and 10 µm spacing. A hydrogen plasma regeneration process was then performed. The sample was placed back in the PECVD chamber and treated with the prior synthesis conditions without the presence of methane. Then, another long-term test with a 10 µm gap and 290 V bias was conducted on the regenerated sample, and the current as a function of time is shown in Figure 10. The emission current reaches the 10–100 µA level. We postulate that the plasma treatment removes undesirable impurities that may have attached to the surface and replaces them with hydrogen termination, which reduces the surface electron affinity [10].

Current–voltage results in Figure 11 correspond to the CNT sample shown in Figure 2. Three different tests were performed on the same sample at different locations and they revealed turn-on fields of 10.0 V µm⁻¹ and 10.5 V µm⁻¹ for the first and second forward bias tests, respectively. For the reverse bias test, in which the silver rod was grounded and the CNT sample was positively biased, the sample turned on at a slightly higher field of 12.0 V µm⁻¹ for the third test under reverse conditions.
bias. Maximum currents of 7.39 pA, 8.39 pA and 3.24 pA were recorded at 200 V during ramp-up for the first, second and third tests, respectively. In general, reverse bias tests exhibited higher turn-on fields and lower currents at equivalent voltages. We note that the reverse bias case involves a different underlying discharge mechanism in which field emission from diamond is excluded, and instead, volumetric breakdown of the air dominates. The current was quite stable in the first 12 s period for the CNT sample, as indicated by the current versus time plot in figure 12. The stability of the current shown in figure 12 confirms initial CNT-to-substrate adhesion. The testing circuit was frequently shortened for times longer than this initial period. The short circuits were likely the result of CNTs that broke away from the substrate under strong electric fields. In any case, CNTs exhibited significantly smaller currents than the HGPD under similar voltages.

4. Conclusions

An HGPD film and CNT array were grown by plasma-enhanced chemical vapour deposition, and two-terminal current–voltage experiments were performed in air under atmospheric pressure and room temperature. The results indicate that an activation process enables low turn-on voltage and sustainable microampere currents for the HGPD sample. Before the activation process, the HGPD sample exhibited relatively poor performance. After activation, ionized atmospheric air at voltages below 350 V while providing sustainable microampere currents over a 40 h time period. A recommended working region was identified between the electrical breakdown curve and the turn-on voltage curve for microscale ion generation. The ionization ability of the HGPD film can be regenerated by a hydrogen plasma treatment. The tested CNT samples show considerably smaller currents than those of HGPD under the same experimental conditions. The fact that diamond has a strongly bonded crystal structure and excellent mechanical and chemical properties makes it an attractive material for generating large quantities of ions at low-voltages.

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