World Academy of Science, Engineering and Technology
International Journal of Mechanical and Mechatronics Engineering
Vol:7, No:2, 2013

Spark Breakdown Voltage and Surface Degradation of Multiwalled Carbon Nanotube Electrode Surfaces

M. G. Rostedt, M. J. Hall, L. Shi, R. D. Matthews

***Abstract*—**Silicon substrates coated with multiwalled carbon nanotubes (MWCNTs) were experimentally investigated to determine spark breakdown voltages relative to uncoated surfaces, the degree of surface degradation associated with the spark discharge, and techniques to minimize the surface degradation. The results may be applicable to instruments or processes that use MWCNT as a means of increasing local electric field strength and where spark breakdown is a possibility that might affect the devices' performance or longevity. MWCNTs were shown to reduce the breakdown voltage of a 1mm gap in air by 30-50%. The relative decrease in breakdown voltage was maintained over gap distances of 0.5 to 2mm and gauge pressures of 0 to 4 bar. Degradation of the MWCNT coated surfaces was observed. Several techniques to improve durability were investigated. These included: chromium and gold-palladium coatings, tube annealing, and embedding clusters of MWCNT in a ceramic matrix.

***Keywords*—**Ionization sensor, spark, nanotubes, electrode, breakdown.

I. Introduction

FOR gas ionization sensors [1] and spark breakdown spectrometers [2], it is thought that a spark discharge event typically passes through three distinct, sequential discharge events: breakdown, arc phase and glow phase. Breakdown is characterized by a high voltage that electrically breaks down the gas mixture in the electrode gap creating a conductive channel of ionized gas through which a current passes. Pashchen in 1889 outlined the electrical breakdown characteristics of gases [3]. He proposed that the breakdown voltage was a product of electrode gap and gas pressure (actually density), or V= f(pd), where p is the pressure and d is the gap distance. This became known as Paschen's Law. For breakdown in air with small gaps on the order of millimeters between smooth flat electrodes, an approximate estimate for the breakdown voltage is: V = 30pd + 1.35 kV, where d is in centimeters, and p is in atmospheres. Many fundamental studies of breakdown behavior have been conducted. Some of these studies are summarized by Maly [4], and have found that breakdown voltage can also depend upon electrode shape and roughness, dust, radiation, and gas composition.

M. G. Rostedt is currently an officer in the U.S. Navy.

M. J. Hall is a Professor in the Department of Mechanical Engineering at the University of Texas at Austin (corresponding author e-mail: mjhall@mail.utexas.edu).

L. Shi is a Professor in the Department of Mechanical Engineering at the University of Texas at Austin (e-mail: lishi@mail.utexas.edu).

R. D. Matthews is a Professor in the Department of Mechanical Engineering at the University of Texas at Austin (e-mail: rdmatt@mail.utexas.edu).

Strong electric fields are desirable for operation of not only gas ionization sensors [1] and spark breakdown spectrometers [2], but also DNA separators [5] and field emission displays [6]. There has been interest to exploit the enhanced local electric field strengths at the tips of multiwalled carbon nanotubes (MWCNTs) for these applications.

It has been shown, for example, that electrical breakdown of the gases between MWCNT electrodes may occur at lower applied voltages than for uncoated electrodes [1], making MWCNT electrodes potentially useful for highly sensitive gas ionization sensors. Their aspect ratio, specifically tip geometry, is the primary factor that makes CNTs applicable for reducing breakdown voltage. The sharp tips of the CNTs create a high localized electric field relative to the spatially averaged field between two electrodes. When CNTs are present, the local field is multiplied by β, the field enhancement factor. Base on the Fowler-Nordheim model of electron emission [7], the factor β is approximately equal to 1/r, where r is the tip radius of the emitter.

The high localized field also enhances field emissions. During field emission, an electron tunnels out of a material due primarily to the electric field, with no help from thermal energy. Their locally strong electric field makes CNT's excellent field emitters. Bonard et al. [8] further concluded that multi-walled, closed end tips are desirable for obtaining low operating voltages and long lifetimes in field emission applications.

Several studies have cited the use of CNTs to reduce breakdown voltage. Rosen et al. [9] successfully demonstrated that single-walled (SW) CNTs could be used to reduce the breakdown voltage of an unknown gas by approximately 30 % in gas discharge tube (GDT) surge protectors. The lifetime of the CNTs was improved by annealing them in a vacuum furnace. Modi et al. [1] reported the reduction of the breakdown voltage of air by approximately 63% at separation distances of up to 160μm in their study of CNTs application to gas ionization sensors. Hui et al. [10] conducted numerous studies on the application of MWCNTs to reduce breakdown voltage in gas ionization sensors. They cited the corona discharge mechanism as the cause of breakdown. There is, however, a lack of understanding regarding the effect of MWCNTs on breakdown behavior, and little is known about MWCNT electrode durability with repeated spark breakdown.

Here, we report a systematic experimental investigation of the effect of MWCNTs on the breakdown voltage with a focus on the MWCNT electrode durability. Several techniques were investigated to improve the durability of the MWCNT

electrode. These techniques include chromium and gold-palladium coatings, tube annealing, and embedding clusters of MWCNT in a ceramic matrix. The following sections describe methods for growth and characterization of MWCNT electrodes, and experiments to test breakdown and durability of the MWCNT electrodes.

II. Synthesis and Characterization of Carbon Nanotube Electrodes

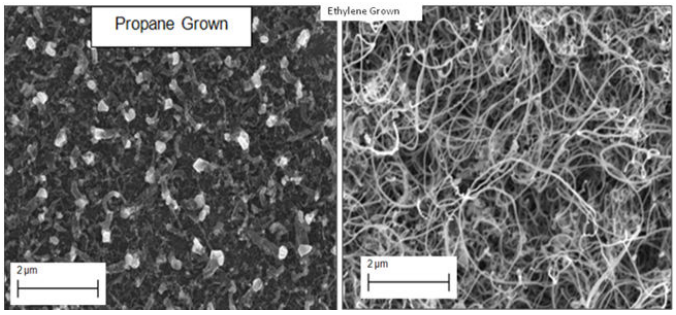
MWCNTs grown using chemical vapor deposition (CVD) require a catalytic metal to act as a nucleation site for tube growth. It has been shown that the most effective metals upon which to form ordered carbons are iron, nickel and cobalt [11]. These metals form ordered carbons for three primary reasons: their catalytic ability to decompose hydrocarbons at high temperatures (CxHy → Cx+Hy), their ability to form metastable (unstable) carbides, and fast diffusion of carbon over/through these metals. All three of these mechanisms together create a process of diffusion around the metals and precipitation of carbon directly onto the metals [12].

The chemical vapor deposition (CVD) method reported by Delzeit et al. [13] for MWCNT growth was adopted in this work. The synthesis was conducted at high temperatures, using a tube furnace setup. The quartz tube, through which growth gasses were flowed, was 25mm in diameter. Two 200 mm long quartz boats held the silicon wafer electrode samples during growth.

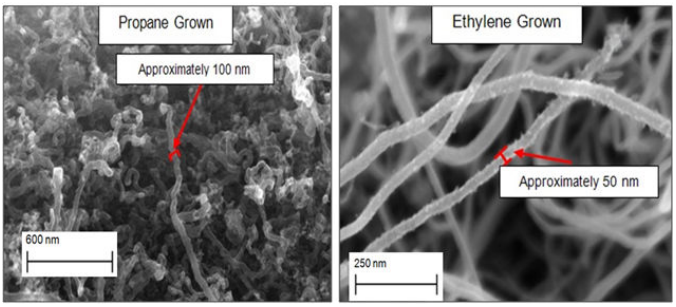
Silicon wafers of 150mm diameter, 600µm thick, [100] orientation were selected as the growth surface. Each wafer was cut into 6 x 6mm pattern pieces for the MWCNT growth and testing. After cutting, the wafer pieces were cleaned and coated with 20nm of 99.95% pure aluminum followed directly by 10nm of 99.95% pure Fe using an electron beam evaporator.

The MWCNTs were synthesized by placing up to 15 samples in a quartz boat which was then placed inside the tube and tube furnace. Argon (99.998% pure) was flowed at 1000 sccm through the tube while it was heated to 700-850°C depending on selected growth conditions. After 10 minutes at 700-850°C to equilibrate, the flow was switched to 1000 sccm of either LPG grade propane or ethylene (chemical purity, 99.0%) for 10-15 minute duration, with the temperature held constant. The flow was then switched back to argon at 1000 sccm allowing the furnace to cool to below 300°C before the samples were removed.

The diameters of the synthesized MWCNTs were measured using SEM. It was found that the diameters of the tubes ranged from ~20-200nm, depending on position in furnace and gas used. Diameters of this size (compared to diameters <20nm for SWCNTs) indicate the growth of multiwalled carbon nanotubes as was expected based on the growth method chosen. Fig. 1 shows SEM images that highlight the differences between propane and ethylene grown MWCNTs. As can be seen, the density of the ethylene tubes was much greater than that of the propane tubes. The ethylene tube diameters were typically below 100nm whereas the propane tube diameters were typically greater than 150nm. It was unclear why the CNT growth was different for the two hydrocarbons. On the other hand, the difference in molecular size (propane C_3H_8, ethylene C_2H_4) leads to different thermal breakdown temperatures. For example, propane has a higher auto-ignition temperature of 452°C compared to ethylene's auto-ignition temperature of 430°C [9]. Furthermore, the propane was a low purity LPG that contained trace amounts of other gasses, whereas the ethylene was high purity (99.0%).



(a)



(b)

Fig. 1 (a) Uncoated propane and ethylene grown MWCNT's (b) Diameters of uncoated propane and ethylene grown MWCNTs

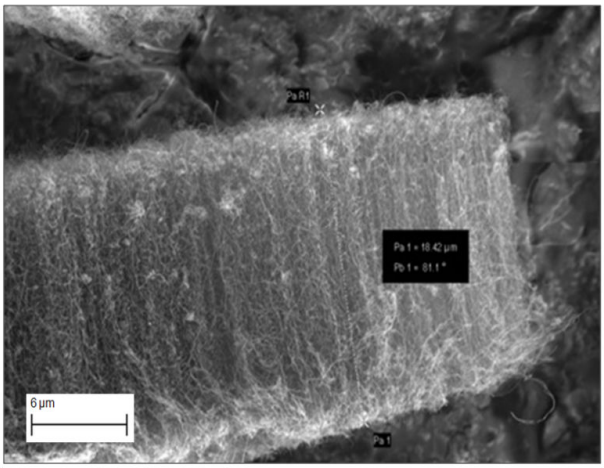


Fig. 2 Side angle view of MWCNTs scraped off substrate surface The two small black boxes in the image are artifacts of the SEM image display

Upon first inspection, it appeared that the growth directions of the MWCNTs were randomly oriented. To characterize tube height, tubes were scraped off the substrates and imaged from a side angle as shown in Fig. 2. It was found that the MWCNTs were very tightly packed. This packing forced the tubes to generally grow perpendicular to the substrate, with an average growth height of 15-20 μm, but the tips of the tubes where randomly oriented. It was concluded that the general growth direction was aligned, but the specific tip alignment of the tubes could not be controlled with this growth method.

III. Breakdown Voltage Measurements

The breakdown voltage testing apparatus made use of components common to a modern automotive ignition system. A schematic of the testing setup is shown (Fig. 3). Components included an ignition coil and ignition module.

A function generator triggered the spark discharge; it sent a square-wave with 5V amplitude to the ignition-module at a user specified frequency ranging from 0.5 Hz to 10 Hz. The ignition module interrupted the current flow to the coil which triggered the spark. A Tektronix P6015A 1000x high-voltage probe and a Tektronix TDS 1002B oscilloscope were used to measure the time-resolved voltage signal from the coil output.

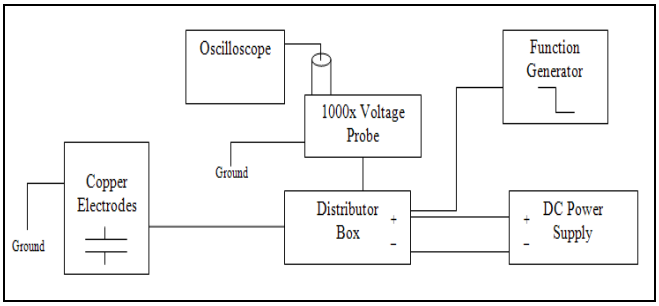


Fig. 3 Breakdown voltage testing schematic

It was found that the breakdown voltage was the same whether one or both of the spark electrodes had the MWCNT coating, thus, for most of the testing only one MWCNT electrode, mounted on a copper plate was used. This was usually the ground electrode. The other (positive) electrode was a copper rod of square cross-section approximately 2 x 2 mm. The CNT electrode was fixed to the large flat plate electrode using electrically conductive copper tape. To accurately set the distance between the electrodes, they were mounted in a fixture attached to a micrometer stage (Fig. 4).

The high-pressure tests were conducted in a constant-volume pressure vessel having optical access through two large quartz windows. The same top electrode used for the other breakdown tests was transferred into the pressure vessel. The electrical wires were passed through fittings in the vessel wall. The gap distance was set at 1 mm for all high-pressure testing.

Voltage data from the oscilloscope were acquired using Labview software. The breakdown voltage was calculated as the average of the first 16 sparks per MWCNT electrode sample and averaged for several different nominally identical electrodes. A standard deviation in measured breakdown voltage was calculated based on the group of electrodes tested.

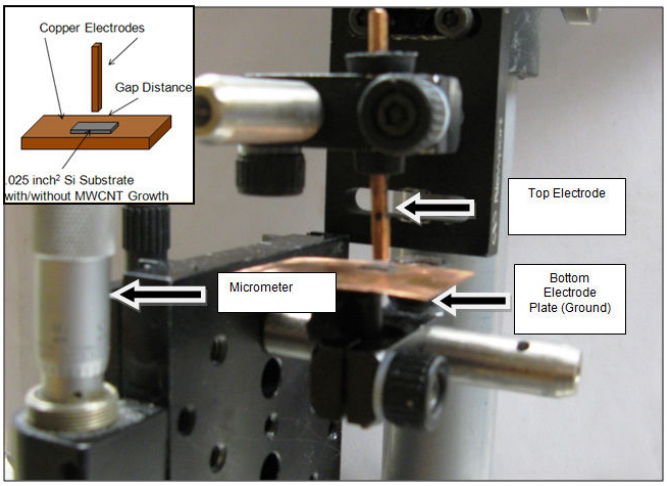


Fig. 4 Copper electrodes and micrometer stage

The percentage reduction in breakdown voltage was calculated by dividing the initial MWCNT breakdown voltage by a reference breakdown voltage. The reference voltage was defined as the average breakdown voltage of a bare wafer for the same separation distance. If tests were conducted on different days, a new reference was used to account for variations in air temperature and humidity.

A. Breakdown Voltage of Uncoated Electrodes

Fig. 5 shows the measured percentage reduction in breakdown voltage for both uncoated propane and ethylene grown MWCNTs at a gap distance of 1mm, relative to a smooth silicon wafer with no MWCNT growth at the same gap distance. A breakdown voltage reduction of approximately 30-50% was achieved, depending on specific growth conditions and gas used. To minimize precision uncertainties, each data point was the average of at least four tested MWCNT electrode samples grown under the same conditions. It was found that growth time and temperature did not significantly affect breakdown performance as long as growth times were kept between 10-15 minutes and temperatures between 700-750°C.

The ethylene grown MWCNTs had a higher percent reduction in breakdown voltage than the propane grown MWCNTs. This was believed related to the differences in diameter and tube density as shown in Fig. 3. It is thought that the smaller diameter and increased density of tubes on the ethylene samples enhanced the localized electric field strength as Mahdy [14] computationally modeled. Because of their superior performance, ethylene grown tubes were used for all other tests.

B. MWCNT Coating Process

Various coating methods and materials were studied in an effort to increase the durability of the MWCNTs during the

spark event. Magnetron Sputter Coating was used to coat MWCNTs with metal layers of varying thickness in attempts to improve electrode durability. The metals selected were chromium (Cr), gold-palladium (Au/Pd) and platinum-palladium (Pt/Pd). Approximately 10 nm thickness provided a uniform coat with not gaps. Chromium, unlike the other metals, oxidizes after a short time in air (approximately 30 minutes). It was thought that this oxidation layer may help improve the thermionic emissions of the CNTs based on previous research [15].

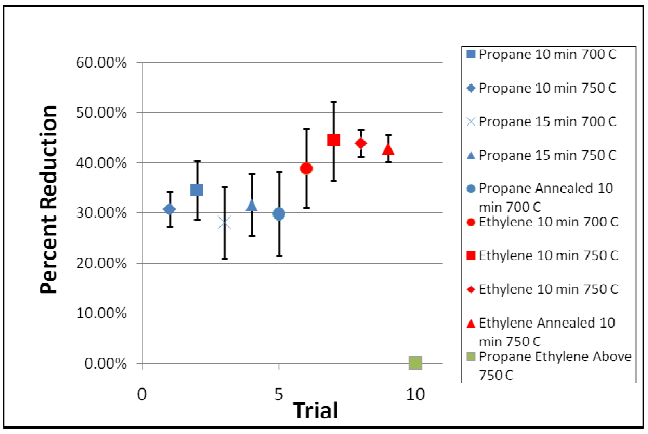


Fig. 5 Average percent reduction and standard deviation of breakdown voltage (1mm gap, uncoated samples)

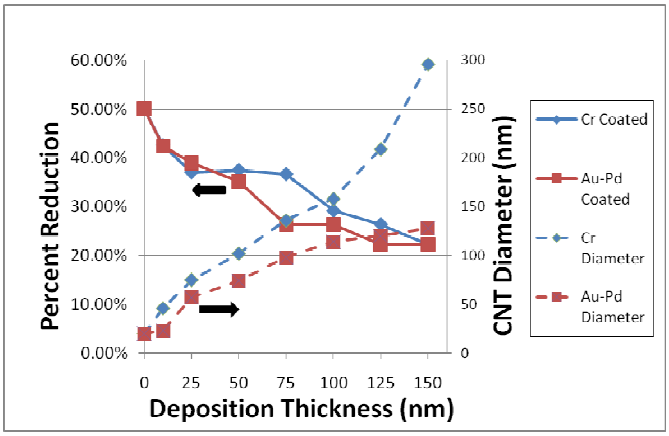


Fig. 6 Average percent reduction of breakdown voltage (1mm gap) and MWCNT diameter vs. deposition thickness of metal coating

C. Breakdown Voltage of Coated Samples

Fig. 6 shows the breakdown voltage of ethylene grown MWCNT's with metal coatings of chromium (Cr) and gold-palladium (Au-Pd). Each data point represents at least 4 tested samples. As the thickness of the metal deposited was increased, the diameters of MWCNTs increased, accordingly. The diameter change was measured by SEM. As the deposition thickness was increased, the percent reduction in breakdown voltage also decreased. The reduced performance with increased deposition thickness correlated with the diameter of the coated MWCNTs. The larger diameters reduced the field enhancement effect at the CNT tips. The chromium coated MWCNTs had a larger diameter than the gold-palladium coated MWCNTs, but the chromium coated tubes exhibited similar or greater percent reduction in breakdown voltages relative to the gold-palladium coated tubes. This may have been due to the tendency of chromium to oxide after a short time (approximately 30 minutes). The oxide layer lowers the work function of the CNTs as Jin et al. [15] reported.

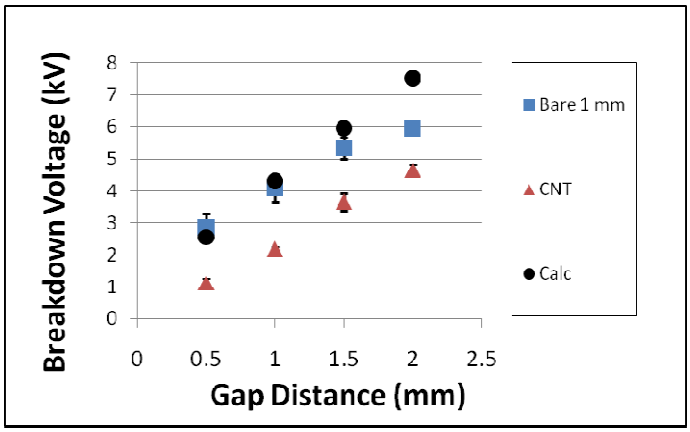


Fig. 7 Breakdown voltage vs. gap distance

D. Breakdown Voltage vs. Electrode Gap Distance

The bare electrode and MWCNT coated electrode breakdown voltages were measured over a small range of gap distances at atmospheric pressure. Results are presented in Fig. 7. The theoretical breakdown voltage is also shown. It was calculated using $V = 30pd + 1.35$ kV. For all of the gap distances the MWCNT breakdown voltages were lower than the bare electrode breakdown voltages and increased linearly with gap distance. The breakdown voltage of the bare substrate did not increase linearly with gap distance, deviating from theory. At 0.5 and 1mm distances, the breakdown voltages of the bare substrate matched the calculated theoretical values within the statistical uncertainty of the measurements. At gap distances of 1.5 and 2mm, however, breakdown voltages were somewhat lower than the calculated theoretical values. The difference was attributed to surface effects. The theoretical values assume infinitely long and completely smooth electrodes. For larger gap distances spatial non-uniformities in surface deposits and surface irregularities may have a greater effect than at smaller gap distances.

IV. Breakdown Voltage vs. Pressure

Fig. 8 shows the breakdown voltage of uncoated MWCNT electrodes at 1mm gap distance for gauge pressures from 0 to 4bar. These measurements where conducted using the pressure vessel. The breakdown voltages of the MWCNT electrodes were linear with pressure and lower than those of the bare electrodes. The theoretical breakdown voltages are also shown in the figure. The bare electrode breakdown voltages (triangle symbols), once again, were lower than the theoretical values, most likely, due to electrode and substrate surface effects.

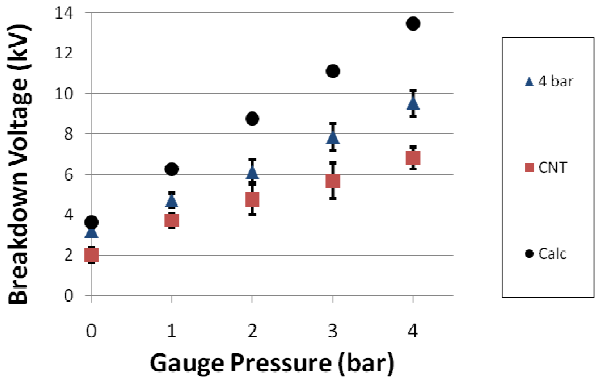
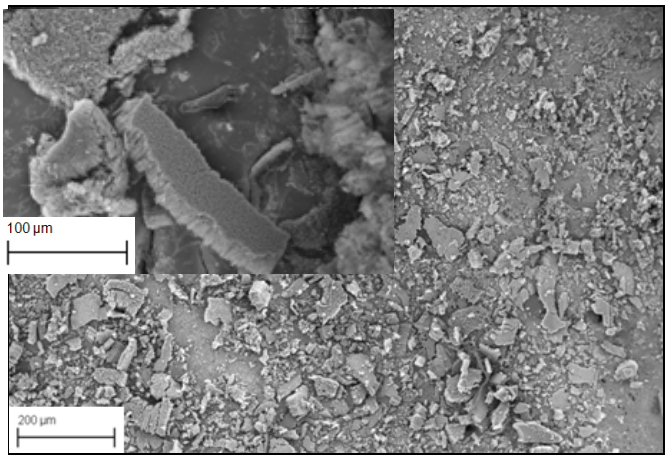
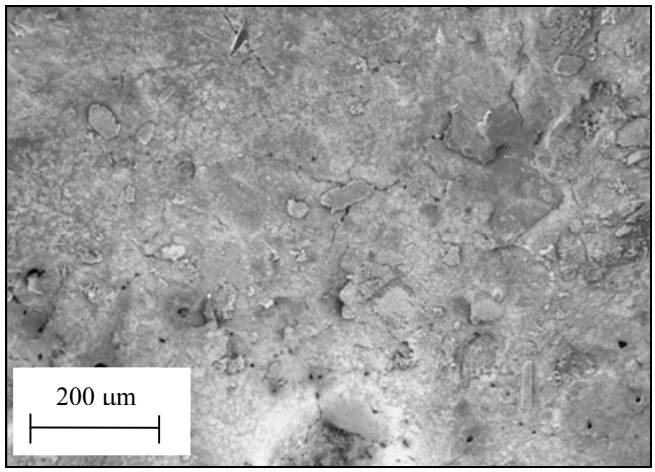


Fig. 8 Breakdown voltage vs. gauge pressure (1mm gap)



(a)



(b)

Fig. 9 (a) MWCNT/ceramic mix before testing (b) MWCNT/ceramic mix after prolonged spark testing

V. Durability of MWCNT Electrodes

Annealing the MWCNTs was examined based on Modi et al. [1] reporting improved durability in gas discharge sensors with annealed CNTs. The annealing was conducted in a vacuum furnace at 600, 900 and 1200°C for 1 hour. Each electrode tested had an initial breakdown voltage reduction (first 16 sparks) of ~ 40-50%, but after 600 sparks, all samples were only reducing the breakdown voltage ~10%. The breakdown voltage of all of the samples changed at close to the same rate. This diminishing effect of the nanotubes was the result of surface ablation of the CNTs.

A. Durability of Ceramic Matrix Electrodes

An idea to possibly improve electrode durability was to embed the MWCNT material in a ceramic paste, which when cured would provide the high temperature and strength properties of the ceramic. Fig. 9 shows SEM images of MWCNT/ceramic matrix electrodes before and after spark testing. As can be seen in Fig. 9 (a), the MWCNTs when mixed with the ceramic were not individual tubes, but rather an inhomogeneous mixture of nanotube clumps embedded in the ceramic matrix. These clumps, resembling flakes of MWCNTs, densely populated the surface of the untested electrode samples. Crushing these clumps to smaller sizes was attempted, but it was not possible to separate them into individual tubes.

Fig. 9 (b) shows that after prolonged spark testing, the density of the MWCNT flakes was significantly reduced. This suggests that the flakes were destroyed during the spark event. However, the crater formations in the nanotube coating observed on the silicon electrodes were not present on the ceramic. The ceramic did change color, however, in a way that suggested intense localized heating.

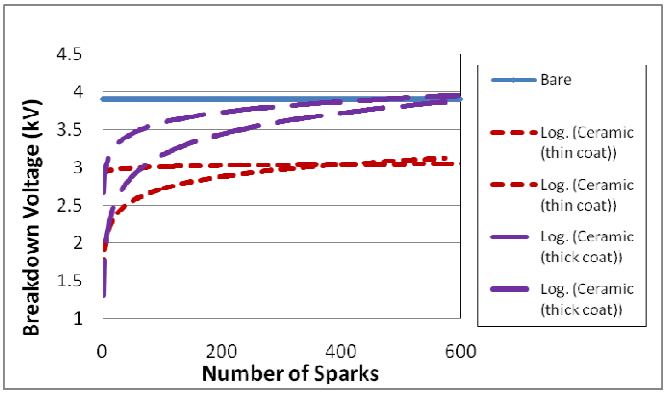


Fig. 10 Durability of MWCNT/ceramic mix

The breakdown voltage vs. number of sparks for the MWCNT/ceramic matrix is shown in Fig. 10. Various MWCNT/ceramic mix thicknesses where applied to electrode samples. The thinner ceramic coatings ("thin coat" in Fig. 10), which were approximately 300µm in thickness, showed a clear reduction in breakdown voltage with little degradation through 100s of sparks. When the thickness of MWCNT/ceramic matrix was increased to between 500-600µm ("thick coat" on the plot), the ability to reduced breakdown voltage deteriorated more rapidly. A thick coating of ceramic mix would exhibit a low initial breakdown voltage, but as testing continued the tubes along the surface degraded quickly, leaving behind only insulating material. As a consequence, the spark would stop

striking the center of the sample and begin to strike an electrically conductive exposed corner of the silicon wafer or the bottom plate copper electrode with breakdown voltage increasing as a result. The thinner coatings had better electrical conductivity through the bulk of the material, as a result, the spark continued to form between the positive copper electrode and the ceramic matrix. Eventual degradation of the tubes resulted in the observed gradual increase in breakdown voltage over 6000 sparks as is shown in Fig. 11.

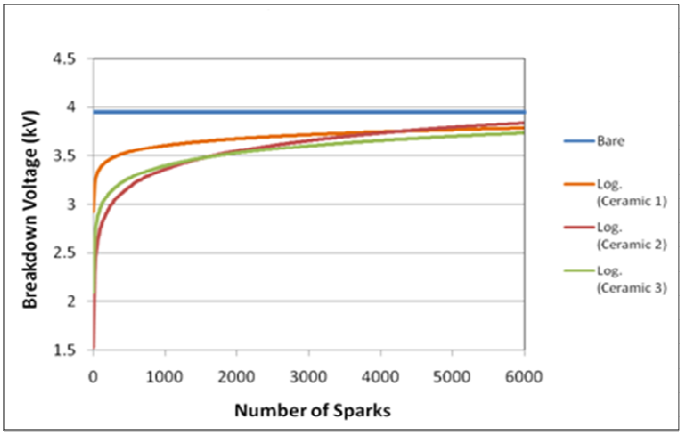


Fig. 11 Durability of MWCNT/ceramic mix over 6000 sparks

VI. Conclusions

Spark breakdown voltages of electrodes coated with MWCNTs were studied. The MWCNTs were synthesized on a silicon wafer surface with a chemical vapor deposition (CVD) technique using either ethylene or propane as the carbon source. The MWCNT tubes were characterized based on their morphology and tube diameter using SEM. Ethylene was found to produce a more uniform, higher density MWCNT film with diameters between 20-100 nm, when growth temperatures were kept under 750°C. Propane grown MWCNTs were lower in density of coverage and had larger diameters (100+nm). This may have been linked to its low purity and possibly different thermal decomposition mechanisms for the hydrocarbons at the growth temperatures. The MWCNTs generally grew perpendicular to the growth surface due to the high tube density, but the individual tube tips were not straight or oriented in a single direction.

The ethylene grown MWCNTs reduced the initial breakdown voltages by 30-50% due to the high localized electric fields created by the small diameter nanotubes. Field emission may also play a role in the breakdown reduction. Along with the lower breakdown voltage obtained with the MWCNTs, the spark duration increased. This is consistent with prior studies that confirmed increases in spark duration as gap resistance is reduced [16]. The MWCNTs were found to reduce breakdown voltages over gap distances of 0.5 mm to 2 mm in air and gauge pressures of 0 to 4 bar. The smaller diameter, more densely packed tubes were found to produce a greater reduction in breakdown voltage.

Destruction of the MWCNTs, resulting in tube vaporization and crater formation, occurred with each spark event. This was due to the high temperatures during the arc phase of spark discharge and/or resistive heating of the MWCNTs during arc-phase electron emission. In an effort to reduce this degradation, metal coatings of chromium (Cr) and gold-palladium (Au-Pd) with thicknesses ranging from 10nm to 150nm were applied. These coatings did not improve the durability of the MWCNTs. These coatings increased the breakdown voltage; correlating with the observed increase in tube diameter due to the coating. Annealed MWCNTs exhibited no improvement in durability.

A MWCNT/ceramic matrix was shown to improve the electrode durability when the matrix was thin enough (approximately 300 μm) to remain electrically conductive. Extended tests were conducted to determine the durability limits of the MWCNT/ceramic matrix. The ceramic matrix samples exhibited an approximately 10X longer lifetime over non-ceramic mix samples, however, degradation of the MWCNTs still occurred.

References

[1] Modi, A., N. Koratkar, E. Lass, B. Wel, P.M. Ajayan 2003, Nature, 424:171.
[2] Nassef, O.A. and H. E. Elsayed-Ali 2005, Spectrochimica Acta B: Atomic Spectroscopy, 60: 12: 1564.
[3] Paschen, F. 1889, Wied. Ann., 37: 69.
[4] Maly, R. 1984, Fuel Economy in Road Vehicles Powered by Spark Ignition Engines, G.S. Springer, New York.
[5] Xu, Y. and S-F-Y Li 2006, Electrophoresis 27: 20: 4025.
[6] N. S. Lee and J. M. Kim 2001, Diamond and Related Materials, 10: 1705.
[7] Sarrazin, P. 2005 Carbon Nanotubes: Science and Applications, editor: M Meyyappan, CRC Press, New York.
[8] Bonard, J.M., J.P. Salvetat, T. Stockli, L. Forro, A. Chatelain 1999, Applied Physics A, 69: 245.
[9] Rosen, R., W. Simendinger, C. Debbault, H. Shimoda, L. Flemming, B. Stone, O. Zhou 2000, Applied Physics Letters, 76: 1668.
[10] Hui, G., L. Wu, M. Pan, Y. Chen, T. Li, X. Zhang 2006, Measurement Sci. and Tech., 17: 2799.
[11] Derbyshire, F. J., A. E. B. Presland, D. L. Trimm 1975, Carbon, 13: 111.
[12] Sinnet, S.B., R. Andrews, D. Qian, A. M. Rao, Z. Mao, E. C. Dickey, F. Derbyshire 1999, Chemical Physics Letters, 315: 25.
[13] Delzeit, L., C. V. Nguyen, R. M. Stevens, J. Han, M. Meyyappan, 2002, J. Phys. Chem. B, 106: 5629.
[14] Mahdy, A.M., H.I. Anis, S.A. Ward 1998, IEEE Trans. on Dielectrics and Electrical Insulation, 5: 612.
[15] Jin, F., Y. Liu, C.M. Day, S.A. Little 2006, Carbon, 45: 587.
[16] Lee, M., M.J. Hall, O.A. Ezekoye, and R.D. Matthews 2005, Society of Automotive Engineers, Paper 2005-01-0231.