Application of carbon nanotubes as electrodes in gas discharge tubes

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Gas-tube protector units are used in telecom network interface device boxes and central office switching gears to provide protection from lightning and alternating current power cross faults on the telecom network. Current gas discharge tube (GDT) protector units are unreliable from the standpoint of mean turn-on voltage and run-to-run variability. Molybdenum electrodes with various interlayer materials were coated with single-walled carbon nanotubes and analyzed for both electron field emission and discharge properties. A mean direct current breakdown voltage of 448.5 V and a standard deviation of 4.8 V over 100 surges were observed in nanotube-based GDTs with 1 mm gap spacing between the electrodes. The breakdown reliability is a factor of 4–20 better and the breakdown voltage is ~30% lower than the two commercial products measured. The enhanced performance shows that nanotube-based GDTs are attractive overvoltage protection units in advanced telecom networks. © *2000 American Institute of Physics.* [S0003-6951(00)03613-5]

Gas discharge tube (GDT) protectors, usually consisting of two electrodes parallel to each other in a sealed ceramic case filled with a mixture of noble gases, are one of the oldest methods used to protect against transient overvoltages in a circuit.[1] Primarily, GDTs are used in telecom network interface device boxes and central office switching gears to provide protection from lightning and alternating current (ac) power cross faults on the telecom network. Gas tubes are designed to be insulating under normal voltage and current flow. Under large transient voltage, such as from lightning, a discharge is formed between the metal electrodes, creating a plasma breakdown of the noble gases inside the tube. In the plasma state, the gas tube becomes a conductor, essentially short circuiting the system and thus protecting the electrical components from overvoltage damage. Gas tubes are robust, moderately inexpensive, and have a relatively small shunt capacitance, so they do not limit the bandwidth of high-frequency circuits as much as other nonlinear shunt components. Compared to solid state protectors, GDTs can carry much higher currents. However, current GDT units are unreliable from the standpoint of mean turn-on voltage and run-to-run variability. Because of the relatively high electric field required for plasma ignition in conventional GDTs, a small gap distance is often required. Small variability in the gap spacing during processing relates to large variability in breakdown voltage.

Single-walled carbon nanotubes (SWNTs) fabricated by the laser ablation process have a tube diameter of 1–2 nm and a bundle diameter of 10–30 nm.[2] Their geometric properties give rise to a large local electrical field enhancement factor (~1000) and therefore low electron field emission turn-on fields. Recent experiments have reported turn-on electric fields in the range of 1.5–3 V/μm.[3–5] The nanotubes emitters, especially the SWNTs, are capable of producing stable electron emission with a current density exceeding 4 A/cm^2 (Ref. 5) which make them attractive cold-cathode materials for microvacuum electronic applications. As-synthesized SWNTs are in the form of either free-standing mat or powder, unsuitable for device applications. We have processed the raw materials to uniform films by a spray method.[6] Adhesion between the substrates and the films is enhanced by introducing either a carbon-dissolving or a carbide-forming metal interlayer. In this letter, we report the effects of carbon nanotube coating on the performance of the gas discharge tubes. The direct current (dc) breakdown voltages of GDTs fabricated using SWNT-coated electrodes were measured and compared with commercial GDTs. A significant reduction in the breakdown voltage and voltage fluctuation (over 1000 surges) was observed for the nanotube-based GDTs as compared to typical commercial devices.

The SWNT materials used in this study were fabricated using the laser ablation system which has been described elsewhere.[7] The raw material was purified first by reflux in 20% H_2O_2 solution at 100 °C, then by filtration in methanol assisted by ultrasonic agitation.[8] They were then dried under 10^{-6} Torr vacuum.[8] The purified materials were characterized by transmission electron microscopy (TEM) and x-ray diffraction measurements. They were found to contain 80%–90% single-walled nanotube bundles with a bundle diameter of 15–30 nm and average nanotube diameter of 1.4 nm. The impurities included nickel and cobalt catalysts, and graphitic nanoparticles. Figure 1 is a representative TEM micrograph of purified SWNTs. Molybdenum electrodes (3/4 in. diameter disk) were first coated with a thin layer (50 nm) of either platinum, aluminum, or iron using either ion sputtering (Pt) or thermal evaporation (Al, Fe). Purified SWNTs were sprayed onto the substrates[6] (electrodes will be denoted as

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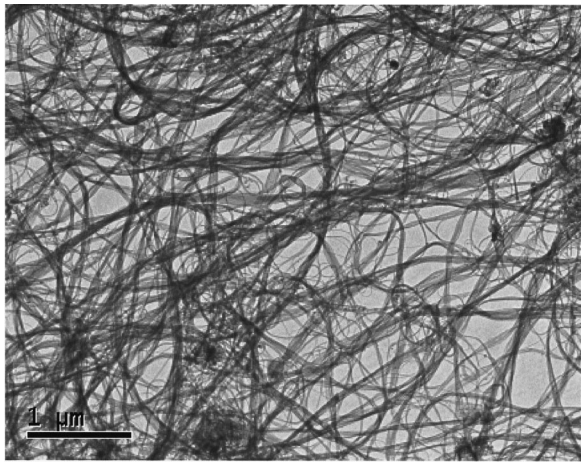

FIG. 1. Transmission electron microscope image of purified single-walled nanotube bundles after purification.

SWNT/M/Mo, M=Al, Fe, or Pt). Some of the electrodes were annealed for 0.5 h at 5×10^{-6} Torr vacuum at 650, 850, and 1150 °C, respectively for the ones with Al, Fe, and Pt interlayer. Measurements were performed on both unannealed and annealed samples.

Electron field emission properties were measured in the parallel plate geometry at 10^{-6} Torr vacuum and a fixed anode-cathode distance of 500 μm. The nanotube-coated electrodes were used as the cathode and plain Mo substrates as the anode. Bipolar GDTs were fabricated with the same type electrodes as both the cathode and the anode. The distance between the electrodes was fixed at 1 mm by a ceramic spacer. The discharge tubes were filled with different noble gas(es) and sealed. The dc breakdown voltage was measured over 1000 surges. For comparison, off-the-shelf commercial GDTs with the same electrode–electrode distance as the nanotube-based devices were also measured.

The field emission data are shown as the *total* emission current (from the 3/4 in. diameter nanotube-coated electrode) versus the applied voltage in Fig. 2. When plotted as $\ln(I/V^2)$ vs $1/V$ (Fowler–Nordheim plot),[9] the data are found to be

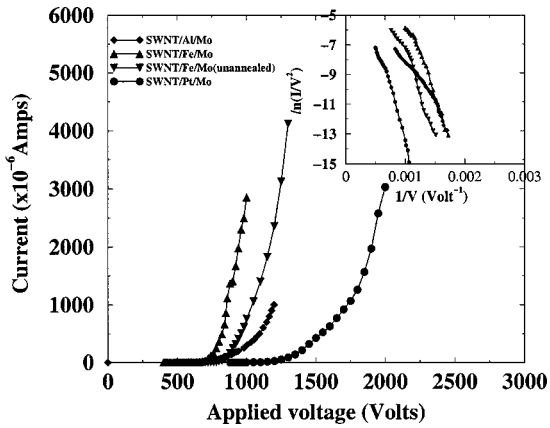

FIG. 2. Total field emission current vs applied voltage measured from SWNT-coated electrodes. The data were collected using the parallel-plate configuration with the nanotube-coated electrode as the cathode and a plain Mo substrate as the anode, and a fixed anode-cathode distance of 500 μm. Inset: The data are plotted as $\ln(I/V^2)$ vs I/V (Fowler–Nordheim plot) and are found to be essentially linear, confirming that the results are indeed due to electron field emission.

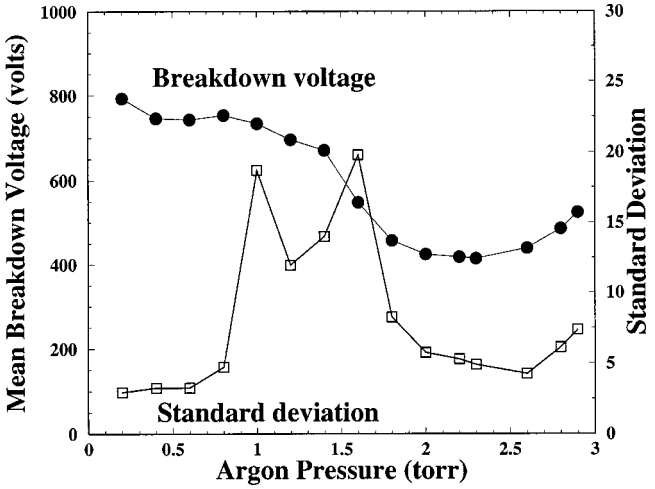

FIG. 3. Mean dc breakdown voltage and standard deviation of a GDT using annealed SWNT/Fe/Mo electrodes at various argon pressure. Ten surges were performed at each Ar pressure.

essentially linear, confirming that the results are indeed due to electron field emission. The emission turn-on voltage (defined here as the voltage for a total emission current of 1 μA) is 600 V (1.2 V/μm) for annealed SWNT/Fe/Mo and SWNT/A1/Mo electrodes, 660 V (1.3 V/μm) for the unannealed SWNT/Fe/Mo electrode, and 1260 V (2.5 V/μm) for the annealed SWNT/Pt/Mo electrode. These values are comparable to the results reported for free-standing SWNT mats[5] and SWNTs deposited directly onto Si wafers.[6] It is worthwhile to note that the present results are based on the *total* current collected over a considerably larger emission area (2.8 cm^2) than those used in the previous studies.[5,3,4] The critical electrical field for 1 mA/cm^2 current density is 1.7, 2.3, 2, and 3 V/μm for the annealed SWNT/Fe/Mo, annealed SWNT/Al/Mo, unannealed SWNT/Fe/Mo, and annealed SWNT/Pt/Mo electrodes, respectively. The difference in the critical emission field between the electrodes with different metal interlayers could be due to the effects of back contact between the nanotube emitters and the substrates or simply sample-to-sample variation.

Direct current breakdown voltage of the GDTs was found to depend strongly on the noble gas and the gas pressure. Figure 3 shows the result from a GDT with two annealed SWNT/Fe/Mo electrodes at various argon pressure. Ten surges were performed at each pressure. The figure shows the mean breakdown voltage and the standard deviation. The most reliable breakdown was observed at 0.5 Torr Ar. The voltage was lower at higher Ar pressure and reduced further when a small amount of neon was added.

Reliability tests were conducted on a GDT fabricated using annealed SWNT/Fe/Mo electrodes. The GDT was filled with 15 Torr argon with neon added and a 1 mm gap between the electrodes. Figure 4(a) shows the dc breakdown voltage of a nanotube-based GDT measured over 100 surges. For comparison, results obtained from two off-the-shelf commercial discharge tubes (with unknown filling gas and gas pressure, but the same gap distance) are plotted on the same graph. The nanotube-based GDT has a breakdown voltage of 448.5 V and a standard deviation of 4.58 V after 100 surges. The GDT from manufacturer 1 has a breakdown voltage of 594 V with a standard deviation of 20 V, while the

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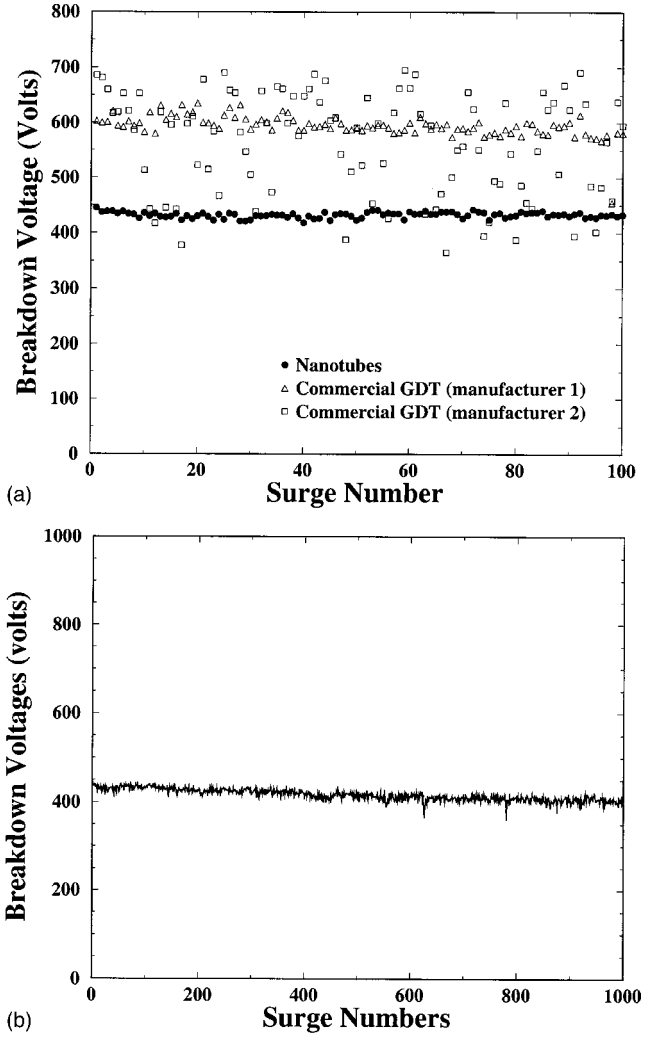

FIG. 4. (a) dc breakdown voltage of a gas discharge tube with SWNT/Fe/Mo electrodes, filled with 15 Torr argon with neon added and 1 mm distance between the electrodes. The commercial GDTs are off-the-shell products with unknown filling gas(es) but the same electrode–electrode gap distances. The breakdown voltage of the GDT with SWNT/Fe/Mo electrodes is 448.5 V with a standard deviation of 4.8 V over 100 surges. The commercial GDT from manufacturer 1 has a mean breakdown voltage of 594 V and a standard deviation of 20 V. The GDT from the second manufacturer has a breakdown voltage of 563 V and a standard deviation of 93 V. (b) dc breakdown voltage of the same GDT with SWNT/Fe/Mo electrodes over 1000 surges. The dc breakdown voltage reduced to 400 V after 1000 surges.

GDT from the second manufacturer has a breakdown voltage of 563 V and a standard deviation of 93 V. The breakdown reliability of the nanotube-based GDT is a factor of 4–20 better and the breakdown voltage is ~30% lower than those of the two GDTs using commercial electrodes. Figure 4(b) shows the dc breakdown voltage of the GDT with SWNT/Fe/Mo electrodes over 1000 surges. The breakdown voltage decreased gradually with an increasing number of surges which is desirable from device protection standpoint. After 1000 surges, the dc breakdown voltage became 400 V.

The plasma breakdown voltage is lower than the field emission turn-on voltage measured in vacuum (1–1.2 V/μm for annealed SWNT/Fe/Mo electrodes). Presently it is not clear whether the breakdown is directly triggered by electrons field emitted from the nanotube coating or due to the locally enhanced electrical field near the nanotube tips. We attribute the enhanced reliability over a large number of surges to the high emission site density and the uniform field enhancement factor ($\beta = E/V$ where E is the effective electric field on the tip and V is the applied voltage) at different emission sites which can be approximated as $1/5r$ where r is the radius of the emitter tip.[9] The emission site density of a SWNT film was previously estimated to be ~1000/cm^2 at the turn-on electrical field.[5]

The dc breakdown voltage of the nanotube coated GDTs decreases gradually with increasing number of surges. The decay is slower in the GDTs using annealed electrodes than for the unannealed electrodes. Gradual decrease in the breakdown voltage is a desirable property from the device protection point of view (in the conventional GDTs, the breakdown voltage usually increases over time due to sputtering and erosion of the electrodes.[1]) After 1000 surges the nanotube-coated electrodes were removed from the devices and were examed by scanning electron microscope. The unannealed electrodes were depleted of SWNTs, while the majority of nanotubes remained intact on the annealed electrodes. The degradation in unannealed electrodes is believed to be caused by pull out of SWNTs under the high electrical field. The difference between the two types of electrodes is consistent with the results from our recent experiments which showed that nanotube films deposited on substrates with Fe interlayers have significantly enhanced adhesion after vacuum annealing at high temperature.[6]

In summary we show that gas discharge tubes comprising SWNT-coated electrodes have significantly improved performance in terms of dc breakdown voltage and reliability over the current commercial GDTs. The lower breakdown voltage and a factor of 4–20 reduction in breakdown voltage fluctuation make carbon nanotube based gas discharge tubes attractive overvoltage protection units for advanced telecommunication networks such as Asymmetric Digital Subscriber Line (ADSL) and High-bit-rate Digital Subscriber Line (HDSL) where the tolerance is narrower than what can be afforded by the current commercial GDTs.

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[1] R. B. Standler, *Protection of Electronic Circuits from Overvoltages* (Wiley, New York, 1989).
[2] A. Thess, R. Lee, P. Nikdaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, and R. E. Smalley, Science **273**, 483 (1996).
[3] P. G. Collins and A. Zettl, Appl. Phys. Lett. **69**, 1969 (1996).
[4] J. M. Bonnard, J. P. Salvetat, T. Stockli, W. A. de Herr, L. Forro, and A. Chatelain, Appl. Phys. Lett. **73**, 918 (1998).
[5] W. Zhu, C. Bower, O. Zhou, G. P. Kochanski, and S. Jin, Appl. Phys. Lett. **75**, 873 (1999).
[6] C. Bower, O. Zhou, W. Zhu, A. G. Ramirez, G. P. Kochanski, and S. Jin, in *Amorphous and Nanostructured Carbon*, edited by J. Sullivan, J. Robertson, O. Zhou, B. Call, T. Allen, Mater. Res. Soc. Symp. Proc. (in press).
[7] C. Bower, S. Suzuki, K. Tanigaki, and O. Zhou, Appl. Phys. A: Mater. Sci. Process. **67**, 47 (1998).
[8] O. Zhou, B. Gao, C. Bower, L. Fleming, and H. Shimoda, Mol. Cryst. Liq. Cryst. (in press).
[9] R. Gomer, *Field Emission and Field Ionization* (Harvard University Press, Cambridge, MA, 1961).

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