

FULLERENES-BASED NANOCRYSTALLINE DIAMONDS

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INTRODUCTION

This study presents the recent results in fabrication of efficient electron field emitters using fullerene-based nanocrystalline diamond - coated carbon nanotubes. Diamond coating provides passive protection as well as active enhancement of emission by lowering electron exit work function. During presented study both, single-walled (SWNT) and multi-walled (MWNT) carbon nanotubes were used to form emitting arrays of nanotubes. Fullerenes were used as a feedstock for formation of nanocrystalline diamond coating over the carbon nanotube arrays.

Carbon nanotubes have been the subject of extensive investigation in the recent years [1– 8] due to their unique mechanical and electronic properties. Electron emission from nanotubes has been investigated by a number of groups worldwide [5–8], but a complete understanding of the emission mechanism is still lacking. Nevertheless, actual field emission displays (FEDs) using nanotubes were fabricated and tested [9]. In order to further improve emission properties by protecting nanotubes from evaporation and by enhancing the emission intensity, a hard, temperature resistant material was needed, having at the same time the ability of lowering electron exit work function. A nanocrystalline diamond was found to be the material of choice.

Nucleation and initial growth of diamond films have been extensively studied, and different procedures and agents were proposed to promote the nucleation, but the mechanism of the process still appears to be elusive. Different solid precursors were used for deposition of diamond and the best results were obtained for nanocrystalline diamond readily obtained from fullerenes by plasma enhanced CVD (PECVD).

EXPERIMENTAL

Multi-walled carbon nanotubes were produced in the DC electric arc between graphite rods. During anode vaporization, about 50% of the carbon is re-deposited on the cathode forming MWNT. The core contains 20-40% MWNT, as characterized by transmission electron microscopy (TEM).

Generally, the tubes are straight with a diameter of 7-12 nm and anywhere from 5-50 layers of concentric graphitic layers. The lengths vary from 0.5 to about 10 microns. The ends are usually capped. In order to separate the MWNT from each other, the core material is ground and sieved to a particle size of less than 50 microns. Purification of MWNT was done by several methods including thermal oxidation under controlled conditions, ultrafiltration, and sedimentation separation.

Single-walled nanotubes were obtained in an "as-produced" matrix of amorphous carbon soot that contains about 7% of C₆₀, C₇₀ and higher fullerenes, in addition to single-walled nanotubes. The production process required the use of a catalyst, so the product also contained nanometer-sized metal particles. SWNTs were characterized by TEM, and were 0.7-2 nm in diameter and several tens of microns long. Unlike the multiple-walled nanotubes, single-walled nanotubes were flexible and often occurred in bundles of up to 20 tubes ("buckybundles"). The as-produced soot contained 10-20% tubes by volume.

Substrates for electron field emission were prepared by spraying the conductive adhesive coating onto the metal foil 0.02 – 0.04 mm thick with one side pre-coated with ground core carbon nanotubes. After drying at room temperature, coupons were heat treated for 15 min at T=150°C, under vacuum. This procedure was repeated 2 to 5 times until a desired thickness of the coating was obtained. Another way to form substrates was to apply a thin coating of colloidal silver onto metal foil and to spray carbon nanotubes on top of it after short drying in air.

Both procedures yielded substrate with good adhesion and electrical conductivity.

Conventional microwave plasma enhanced CVD system with a quartz bell-jar chamber was used for deposition of nanocrystalline diamond. A C₆₀/C₇₀ mixture and as-produced fullerene soot (APFS) were used as precursors for diamond deposition. The experiments were carried out at 9 kPa, either in hydrogen-argon or in hydrogen-helium mixtures. The substrate temperature was

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900°C, and the temperature of the fullerene evaporator was 700°C.

RESULTS AND DISCUSSION

The electron field emission of the samples was measured before and after deposition of diamond. The type of the metal basis (Mo, Cu or Al) did not affect the results of measurements. The obtained results have shown that the emitting surface materials were the most important for the emission characteristics.

Measured data were used to plot emission current-field diagram and to determine the switch-on field. In addition to that, a threshold voltage was plotted against electrode gap to calculate the threshold field. For most of the uncoated samples the switch-on field was between 2 and 2.5 V/μm. After deposition of diamond coating, the values were always lower, in most of the cases by 15%. Single walled nanotubes have shown somewhat better emission characteristics than MWNT. The turn-on field was similar for both groups but emission current measured for SWNT was higher than for MWNT (Fig. 1).

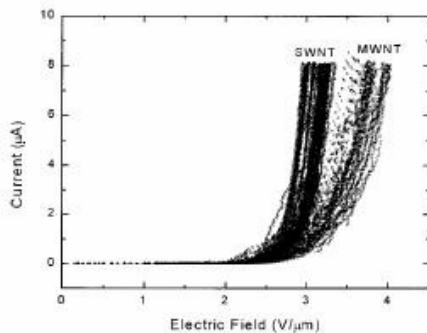


Fig. 1. Electron field emission from SWNT and MWNT arrays before diamond deposition

In both cases the deposition of diamond have visibly improved emission characteristics, mainly by lowering their threshold field from ~ 2.5 V/μm to below 2V/μm (Fig. 2). Figure 3 shows nanocrystalline diamond coating over the substrate of MWNT.

Thus, it could be concluded that in all the examined cases the deposition of nanocrystalline diamond coating over the substrate of sharp emitters, such as SWNT and MWNT arrays,

resulted in improved electron field emission characteristics.

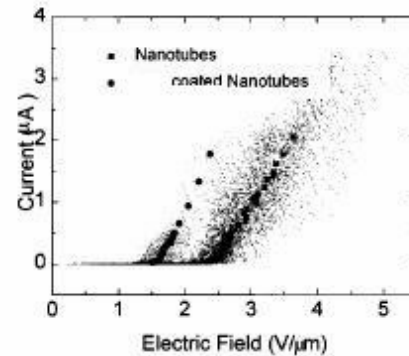


Fig. 2. Electron field emission before and after coating MWNT

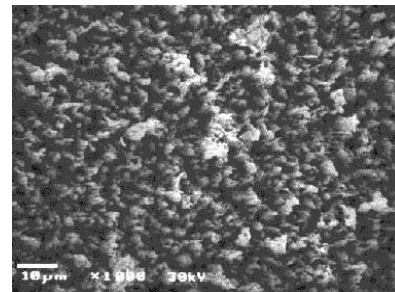


Fig. 3. Diamond coating over the substrate of MWNT.

REFERENCES

1. Iijima S, Ichihashi T. *Nature* 1993; 363: 603.
2. Bernholc J, Roland C, Yakobson B. *Current Opinion in Solid State and Mater. Sci.* 1997; 2: 706.
3. Bethune D, Kiang C, deVries M, Gorman G, Savoy R, Vazquez J, Beyers R. *Nature*, 1993; 363: 605.
4. Kuttel O, Groening O, Emmenegger C, Schlapbach L. *Appl. Phys. Lett.* 1998; 73: 2113.
5. Bonard J et al. *Ultramicroscopy* 1998; 73: 7.
6. Bonard J et al. *Appl. Phys. Lett.* 1998; 73: 918.
7. Bonard J et al. *Appl. Phys.* 1999; A69: 245.
8. Saito Y et al. *Ultramicroscopy* 1998; 73:1.
9. Choi W et al. *Appl. Phys. Lett.* 1999; 75:3129.