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# Enhanced electron emission from tetrahedral amorphous carbon capped carbon nanotube core-shelled structure

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ABSTRACT

Core-shelled composites have been shown to enhance material properties, notably for chemical sensing and biomolecular applications. In this comprehensive study, we show that a simple core–shell structure, made up of tetrahedral amorphous carbon (ta-C) tip-capped onto an aligned dense array of carbon nanotubes (CNT), exhibits superior electron emission properties, having a distinct enhancement in the turn-on field of $<1$ V/μm without any lithography patterning. This is compared to ~2 V/μm for pristine CNT samples. A KrF pulsed laser deposition process was used to deposit high ($>70\%$) sp$^3$ content non-hydrogenated ta-C films of varying thickness for the tip-capping process. Combining scanning electron microscopy images and electron emission testing results, our systematic study shows that first, the thickness of the ta-C can range from 20 to 100 nm and is sufficient to achieve the enhancement effect. However, thicker coatings $>200$ nm will degrade the electron emission. Second, a simple tip-capping is sufficient to achieve the enhancement without the need to encapsulate the entire carbon nanotube.

## 1. Introduction

Recent interests in nanostructured carbon materials have been explosive, on both scientific and technological fronts, due to their extensive range of physical and chemical properties. The common nanostructured materials are sometimes known as carbon nanotubes (CNTs) composites or in some other research work, called core-shelled structures. CNT composites are usually made from dispersion of CNTs into various materials such as polymers [1] and ceramics [2] to enhance the material properties. CNTs have been one of the most common carbon-based material used as the main core since its discovery by Iijima [3]. Owing to the nature of their tubular graphitic structure, CNTs are entailed with exceptional mechanical and electrical properties that arise from its impeccable structure, bonding and chemical stability making them one of the most thrilling materials discovered [4–7]. For the latter, the core–shell structures usually refer to a composite where various materials cover each individual strands of CNT. Core–shell structures usually require a base structure (core) is usually functionalized with either nanoparticles and/or a fully encapsulated film coating (shell). In general, the most common way to obtain core–shell structure of CNT is by using chemical synthesis techniques such as surface modification (functionalization) of the CNT [8]. This functionalization of the CNT is essential as the CNT is chemically stability thus making it inert to chemical reactions. Currently, applications of these core–shell structures in photovoltaics [9], catalysts [10] and electron emitters [11] to name a few have been reported.

Electron emitters refer to devices that can emit electrons through a quantum mechanical tunneling process under an applied electric field. Many researchers have reported high expectations that CNTs are promising field emission cathodes, due to their long and thin structure together with the chemical inertness of the surface tip [12,13]. The inertness allows for unwavering current density emission whilst maintaining their high electrical and thermal conductivities [12–15]. This can bring advantages such as low turn-on field and low-cost production in contrast to Spindt-tips electron emitters [14,16]. Favourable electron emission properties were first reported on “core-shell” structures when carbon ions were deposited on diamond mesa-diode structures [17]. As such, various wide-bandgap semiconductors have been studied where various metal oxides were coated on CNTs to test the electron emission properties [11]. Some materials, such as MgO, were observed to decrease the turn-on field and reduce the field required for saturation current. Other materials, such as SiO$_2$, were observed to do the opposite [11]. In these studies, the thickness of the coatings was shown to play a role though no direct correlation was reported.

One wide-bandgap semiconductor candidate is diamond-like carbon, which usually is made up of amorphous carbon, containing a random mixture of sp$^2$ and sp$^3$ bonds with a mixed cubic (diamond) and hexagonal (graphite) structures. The structural bonds are randomly inter-mixed between each atomic layer. Tetrahedral amorphous carbon (ta-C) is a metastable form of the amorphous carbon containing a significant fraction of sp$^3$ bonds (~80%) with little or no hydrogen content in

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its bulk [4]. While ta-C possesses many properties similar to diamond, such as high hardness, high Young's modulus, chemically inert and wear resistant, it has unique material properties such as negative electron affinity, thus making electron emission at low voltages viable [4]. This physical properties make it possible for this material to withstand ion bombardment and while possesses excellent thermal and electrical conductivity to tolerate high current transmission [4,15,18-20].

Both of these two carbon-based materials have been independently reported as the future of electron emission products for device applications, such as displays and sensors [4,14–16,18–20]. In combining both ta-C and CNT to form nanostructures, unique material properties may be obtained and several researchers have reported varying success. By using the filtered cathodic vacuum arc (FCVA) technique to obtain ta-C films, Teo et al. [21] has shown that 5 μm thick ta-C coatings can be successfully deposited on vertically aligned CNTs. These nanostructures films exhibit excellent damping properties and could be used as shock absorbers [21]. For application as electron emitters, hydrogenated ta-C (ta-C:H) was deposited on CNTs and enhanced electron emission was also reported [22]. However, it was not certain whether the enhancement reported was due to the hydrogen-bonding or otherwise. For non-hydrogenated ta-C coatings, Dimitrijevic et al. showed that a 20 nm thick ta-C on CNT core–shell structures deposited using the FCVA technique has an improved turn-on voltage [15]. However, the electron emission obtained did not seem to follow the Fowler–Nordheim plots. Furthermore, the relationship between the thickness of the ta-C layer and the turn-on field was not reported and no SEM images were shown to better understand the uniformity of the coatings [15].

In this article, we demonstrate a pragmatic yet simple integration of the two carbon-based materials into a nanotube-based core–shell structure, where enhanced electron emission can be obtained without any pre- or post-deposition chemical treatments. In order to test and fabricate electron emission samples, vertically aligned arrays of multi-walled CNTs are blanket deposited on silicon substrates without any lithography patterning. To integrate the two materials, high quality hydrogen free diamond-like ta-C films are deposited using pulsed laser deposition (PLD) instead of FCVA. As such, this article compares between the effects of two different techniques. PLD is another convenient and popular technique as the laser ablation can be tuned to produce various desired ions with a range of kinetic energies. The ability to do so allow good and repeatable control in the formation of desired metastable carbon form, e.g., the sp$^3$ content within a DLC film can be varied [23]. As such, the PLD technique has been widely used to deposit ta-C [24]. In addition, physical properties such as the effects of film thickness on the electron emission properties were systematically studied to understand better this enhancement and described in detail.

## 2. Experimental

### 2.1. Growth of CNTs

A Denton Discovery-18 Magnetron Sputtering System was used to sputter deposit the thin iron (Fe) layer (~7 nm) directly on base silicon Si(100) substrate. The Plasma Enhanced Chemical Vapour Deposition (PECVD) method, using a Plasma Quest Series II, was used to deposit aligned carbon nanotubes. The feed gases hydrogen ($H_2$) and acetylene ($C_2H_2$) were employed at a RF power 100 W and growth temperature of 700 °C. A 20 min growth time was selected and growth was initiated after pre-etching the Fe catalyst with $H_2$ for 10 min within the chamber. The detailed growth mechanism was previously described elsewhere [25–27].

### 2.2. Preparation of core-shelled structure

High sp$^3$ content ta-C film was deposited using a single beam Lambda Physik KrF pulsed excimer laser PLD system at 248 nm wavelength. The target surface, a 99.9% pure carbon, was struck by the laser operating at a frequency of 20 Hz and energy of 200 mJ in a high vaccum ($1 \times 10^{-6}$ Torr) environment. The quality of the ta-C films deposited by the PLD method has been previously described elsewhere [28,29]. In order to study the relationship between the ta-C film and the encapsulated CNT structures, core-shelled nanostructure of varying ta-C thickness were deposited. Due to the difficulties in quantification of cylindrical type of coatings, simultaneous deposition on bare silicon Si(100) substrate was used as a reference where the thickness of the thin film on the substrate was referenced instead. The thickness of the ta-C films ranged from 20 nm, 100 nm, 200 nm, and 500 nm measured from the Si(100) substrate.

### 2.3. Characterization

After deposition, a Philips XL-30 field emission scanning electron microscope (FESEM) operating at a low 5–10 keV was used for surface topographical imaging. A low operating voltage is used to avoid any specimen damage by electron irradiation. The nature of carbon network of the films, especially the sp$^3$ fraction of the ta-C films deposited on the CNTs, was characterized by high resolution X-ray photoelectron spectroscopy (XPS). A Shimadzu Kratos DLD high resolution XPS system utilizing a monochromatic 1486.6 eV Al-Kα source at a constant pass energy of 20 eV was used to study the specimen. The stimulated electron emission test of the CNTs samples was carried out with a custom-designed field emission system, using parallel plate geometry at room temperature. The emitter-to-anode distance was maintained at 100 μm by inserting a polymer film spacer, on which a hole with a fixed area was fashioned to define the total emission area. The chamber was pumped down to a base pressure of $\sim 5 \times 10^{-7}$ Torr. Prior to the field emission test, a reverse bias was applied to check for the leakage current so as to confirm that the electron emission results are due to the arrays and not a few individual carbon nanotubes. The field emission current–voltage (I–V) relationship was obtained by applying a dc field between the sample and anode. Emission current was measured using a Keithley 237 source measurement unit.

## 3. Results and discussion

The SEM images of the as-grown CNTs and the core–shell nanostructures are shown in Fig. 1 and Fig. 2. The cross sectional image of pristine CNTs in Fig. 1 reveals that the CNTs are highly dense and vertically aligned with respect to the silicon substrate. Fig. 2(a) shows the top-view image of the pristine CNTs. In Fig. 2(b), (c), (d) and (e) show the core–shell nanostructures where an equivalent ta-C film was deposited for 20 nm, 100 nm, 200 nm and 500 nm respectively. In Fig. 3, XPS results using the core–shell C 1s spectrum show that there is little or no intermixing and other substrate effects. High resolution analysis further shows that the ta-C film possesses a

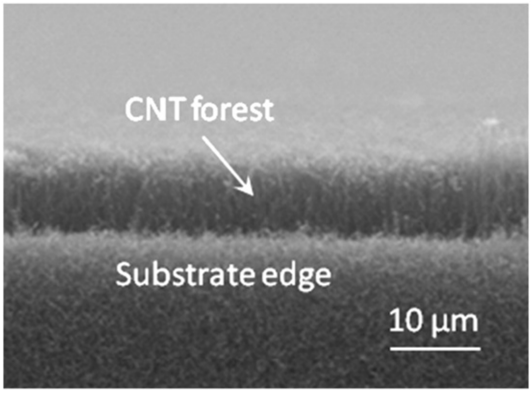

**Fig. 1.** The cross sectional SEM image of the as-grown CNTs, indicating the high density and vertically alignment of the CNTs.