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Oxygen and nitrogen doping in single wall carbon nanotubes: An efficient stable field emitter

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Vertically aligned single wall Carbon Nanotubes (v-SWCNTs) were synthesized by plasma enhanced chemical vapour deposition system. Oxygen and nitrogen molecule inclusion in v-SWCNTs was performed in ultra high vacuum by radio frequency (RF) sputtering system. The creation of defects induced by oxygen and nitrogen plasma ions also drives the formation of different oxygen and nitrogen species at the SWCNTs sidewall surface as well as SWCNTs tips where incorporation is more efficient. The G/D ratio, radial breathing mode and other oxygen and nitrogen characteristic Raman modes were analyzed from Raman spectra. The type of attachments was also interpreted from fourier transform infrared spectroscopy and the electronic 1s core levels of oxygen and nitrogen with carbon in X-ray photoelectron spectroscopy. The effect of oxygen and nitrogen inclusion on the surface of SWCNTs was investigated in terms of its correlation in the enhancement of field emission characteristics. The analysis was done on the comparison of change in field enhancement factor of as-grown SWCNTs and plasma induced O-&N-SWCNTs. The results show drastic enhancement in current density at low turn on field with long term emission current stability. Our results give very unique improvement in field emission display devices using SWCNTs with simple doping effects.

1. Introduction

Doping in carbon nanotubes (CNTs) with foreign atoms has attracted a large attention of the researchers in the last decade [1,2]. It is not only an effective method to alter electronic and mechanical properties of CNTs for optimizing a targeted application but also doped carbon nanotubes can be used as an organic catalysts for energy conversion system, such as water oxidation and oxygen reduction reactions [3,4]. The properties of single wall carbon nanotubes (SWCNT) are dependent of its diameter and chirality. If some dopant of high curvature is incorporated in SWCNT then its properties are enhanced. Comparatively, the impact of doped SWCNTs is greater than that of doped multiwall carbon nanotubes (MWCNTs). Therefore, the doping of oxygen (O_2) and nitrogen (N_2) into SWCNTs intended to enhance the electronic properties of the nanotubes so that they would easily be applicable in electronic devices and other applications [5–8]. The electronic structure of SWCNTs prevents the easy binding of nitrogen than oxygen towards its external surface due to their electronic configurations. The results shown by the previous researchers indicate that the interaction of nitrogen (having triple bond) with SWCNTs is more constructive at open end than its external surface [9,10]. However, the binding of oxygen atoms (having double bond) are more effective at the external surface of SWCNTs. It is still an open question whether oxygen and nitrogen atoms are actually incorporated into the carbon nanotubes lattice or it creates certain amorphous regions within the nanotubes or at the external surface of the nanotubes.

If we consider sp^2 electronic structure of CNT, then it is easy to understand that adsorption of N_2 molecules is more difficult than adsorption of O_2 molecule at the external surface of CNTs. It is now well known that, electronic structure of O_2 is KK $(\sigma^2 s)2$ $(\sigma^2 s^*)^2$ $(\sigma^2 p_z)2$ $(\pi^2 p_x)^2$ $(\pi^2 p_y)^2$ $(\pi^2 p_x^*)^1$ $(\pi^2 p_y^*)^1$ and transferred electron will surely occupy the half-filled anti-bonding orbitals of oxygen molecule and therefore will weaken the O–O bond. Whereas, the electronic structure of N_2 is KK $(\sigma^2 s)^2$ $(\sigma^2 s^*)^2$ $(\sigma^2 p_z)^2$ $(\pi^2 p_x)^2$ $(\pi^2 p_y)^2$

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and the binding orbital of nitrogen molecule is filled, therefore, the transferred electron can't occupy this binding orbital [11,12]. Basically, three distinct types of nitrogen molecules incorporations in graphitic structures exist; pyridinic, quaternary and pyrrolic. The main disparity between pyridinic and pyrrolic defects is associated with the number of contributed electrons in the π-system. The pyridinic nitrogen contributes one electron to the π-system whereas pyrrolic nitrogen contributes with two electrons and therefore no pyrrolic nitrogen atom needs to be located in a pyrrole ring [13]. It is therefore to be noted that for a plane structure, pyridinic, pyrrolic and quaternary nitrogen atoms are in sp^2 hybridized configurations, but as the curvature is increased such as in CNTs, the admixture of sp^3 character is increased with these bonds. In view of the fact that pyrrolic nitrogen atoms are understood to increase the curvature to a higher level and therefore can easily be connected with a stronger sp^3 character [14,15]. We have shown a schematic representation of possible common interaction of oxygen and nitrogen species with carbon atoms in SWCNTs (Fig. 1).

In this work, the as-grown SWCNTs were doped with oxygen and nitrogen using plasma functionalization process. Since, doping of oxygen and nitrogen affects the electron transport characteristics of SWCNTs, therefore, field emission properties of doped SWCNTs were analyzed and it was observed that doped SWCNTs are excellent field emitters for future display devices.

SWCNTs as field emitting material have already possessed many excellent properties such as high field emission, low turn-on field, long lifetime, narrow energy distribution, high brightness and stable emission current due to its small diameter which provides the highest aspect ratio compared with MWCNTs [16–20]. Any system that uses an electron source could potentially host a SWCNT based field emission device. But, for excellent field emitters, an optimal combination of high density array of vertically aligned SWCNTs with large scale control of diameter, length, alignment, orientation and more importantly good adhesion with the substrate is required [21–27]. The most favourable method to achieve the above specific synthesis requirement of SWCNTs is plasma enhanced chemical vapour deposition (PECVD) which can be used to synthesize SWCNTs at very low temperature [28–40].

Therefore, firstly, in this work, we aimed to synthesize vertically aligned SWCNTs with optimum density of array with tight control of diameter and length. For better adhesion with substrate, Fe/Al catalyst coated Si substrates were used. Secondly, the as-grown SWCNTs were doped with oxygen and nitrogen species using plasma functionalization process in order to enhance the field emission characteristic properties of SWCNTs based display devices. Thirdly, field emission studies were recorded using field emission setup and we observed that after doping of oxygen and nitrogen species, the SWCNTs have shown long-term emission current stability and also improvement in the field emission factor. In order to verify enhanced field emission properties of SWCNTs, a comparative study was performed among as grown SWCNTs, oxygen and nitrogen doped SWCNTs.

2. Experimental

2.1. Synthesis of SWCNTs

During synthesis of SWCNTs using PECVD system, Fe/Al coated Si substrate was placed upon a graphite heater fitted inside the quartz belljar chamber of PECVD system (Black Magic 2 inch system, AIXTRON, Cambridge, UK). The chamber was evacuated to a pressure of the order of 15 mbar. Direct current (DC) plasma at a power of 40 W was used, to assist uniform and vertically aligned growth of the SWCNTs. We followed two steps to synthesize the SWCNTs. In the first step, pre-treatment of the Fe/Al substrate was done under hydrogen (H_2) gas atmosphere having continuous flow rate of 750 sccm for 10 min at 450 °C. The temperature was monitored using thermocouple connected to the graphite heater cum substrate holder. In the second step, after pre-treatment, high purity acetylene (C_2H_2) gas at a flow rate of 20 sccm was inserted into the chamber in continuation with increased H_2 flow rate of 1380 sccm. During growth process, the heater temperature was quickly raised from 450 °C to 500 °C. The growth time was kept 15 min. After growth process is over, the samples were then cooled down to normal room temperature.

2.2. Doping process

In order to improve the field emission properties of as-grown SWCNTs, the samples were subjected to oxygen and nitrogen doping using plasma functionalization process for 10 min. The radio frequency (RF) sputtering system used for plasma functionalization process was operated at RF power of 100 W and at a frequency of 13.56 MHz. During plasma functionalization, excited electrons, ions, and free radicals are generated through inelastic collisions between energetic electrons and molecules [41–43]. These plasma

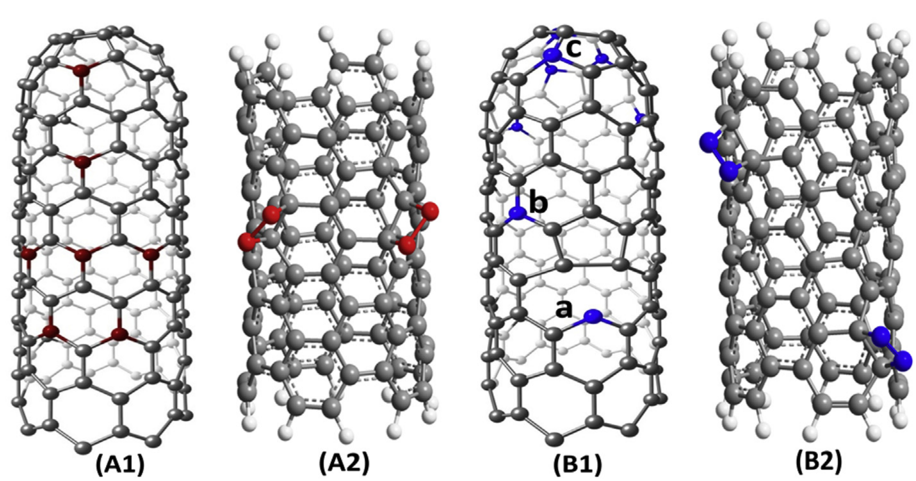

Fig. 1. In SWCNTs, Schematic representation of possible common configuration of (A1) carbon atoms (in grey) with oxygen atoms (in red) (A2) oxygen molecular type interaction with Carbon atoms and (B1) Carbon atoms (in grey) with nitrogen atoms (in blue); the sp2 hybridized (a) pyridinic nitrogen atoms, (b) graphitic and, (c) sp3 hybridized pyrrolic (B2) Nitrogen molecular type interaction with carbon atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)