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Synthesis, structural and field emission properties of multiwall carbon nanotube-graphene-like nanocarbon hybrid films grown by microwave plasma enhanced chemical vapor deposition

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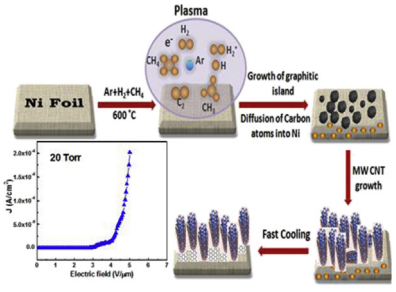
HIGHLIGHTS

- MWCNT-graphene-like nanocarbon hybrid films were synthesized by MWPECVD technique.
- Effect of pressure on the structural and field emission properties has been studied.
- FESEM revealed MWCNT and HRTEM revealed graphene-like nanocarbon film structure.
- Minimum E_T = 3.6 V/μm with β = 3164 has been obtained in the film deposited at 20 Torr.
- Maximum J = 0.12 mA/cm^2 with β = 3356 has been obtained in the film deposited at 5 Torr.

GRAPHICAL ABSTRACT



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ABSTRACT

Multiwall carbon nanotube (MWCNT)-graphene-like nanocarbon hybrid films were directly deposited on nickel substrate without any pre-treatment in a single-step by microwave plasma enhanced chemical vapor deposition (MW PECVD) technique at 600 °C. The effects of hydrogen partial pressure on the growth of MWCNT-graphene-like nanocarbon hybrid films and their structural, morphological and field emission properties were investigated. High resolution scanning electron microscope revealed MWCNT structure. High resolution transmission electron microscope images and Raman spectra revealed graphene-like nanocarbon film. Raman spectra showed 2D, G, D and D + G peaks at approximately 2690, 1590, 1350 and 2930 cm^{-1}, respectively. The minimum threshold field for electron emission was found to be 3.6 V/μm corresponding to 1 μA/cm^2 current density for the MWCNT-graphene-like nanocarbon hybrid film deposited at 20 Torr pressure whereas the maximum current density of 0.12 mA/cm^2 and field enhancement factor of ~3356 was obtained for the sample deposited at 5 Torr pressure.

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1. Introduction

So far carbon is the only material that exists in zero dimension, one dimension, two dimensions and three dimensions. The integration of one dimensional and two dimensional allotropes of carbon may comprise of properties of both the allotropes. One dimension allotrope of carbon, carbon nanotube (CNT) and two dimensional allotrope of carbon, graphene are of significant interest due to their electrical, mechanical and optical properties [1–3]. Recently, a combination of one dimensional carbon nanotube (CNT) to two dimensional graphene give CNT-graphene hybrid materials that have the potential to reduce agglomeration and thereby enhance the electrical properties which otherwise could not be realized using CNT or graphene alone [4–7]. The CNT-graphene hybrid may be CNT rich if graphene is grown by unzipping outer or inner wall of the multiwall CNT (MWCNT) and graphene rich if the CNT stand vertically or spread horizontally on the graphene sheets [8]. CNT-graphene hybrid materials have been used to fabricate electron field emitters [9,10], transparent conductors [11], electrodes for the lithium ion battery and supercapacitor [7,12,13]. Deng et al. [9] demonstrated enhanced field emission properties in the CNT-graphene hybrid prepared by radio-frequency sputtering technique. The CNT-graphene hybrid showed low turn-on electric field of 0.98 V/μm, threshold field of 1.51 V/μm and large field enhancement factor of 3980 with good stability. The integration of sharp edges of graphene along with the high aspect ratio of CNT is responsible for the improvement in field emission properties of CNT-graphene hybrid [5]. Deng et al. [9] further improved the turn-on electric field to 0.73 V/μm by growing graphene flakes on the carbon nanotube arrays by using microwave plasma enhanced chemical vapor deposition (MW PECVD) technique. Koh et al. [10] prepared CNT-graphene hybrid field emitters by electrophoretic deposition method with improved field emission properties compared to CNT. Graphene has acted as connecting particles between the CNT strands and improved the conductivity within the porous CNT network which in turn lowered the turn-on fields of CNT-graphene hybrid films. CNT-graphene composite was used as a transparent conducting material for polymer solar cell and obtained a power conversion efficiency of 0.85 with 86% transmittance [14]. Fan et al. [15] fabricated a 3D like carbon structure with CNT pillars grown in between the graphene layers by CVD method and improved the electrochemical performances of supercapacitor by enhancing the transportation of ions and electrons throughout the electrode matrix. Kim et al. [4] fabricated a 3D like carbon structure with MWCNT-graphene composite as an effective conducting scaffold to enhance the photo-electrochemical water oxidation activity of a hematite film. They reported significant improvement in the photocurrent compared to hematite anode due to the improved charge transfer from hematite particles to a TCO substrate by enlarging the contact area between the scaffold and hematite particles. CNT-graphene hybrid materials have been prepared by a variety of methods including solution process [15], electrophoretic deposition [14], chemical vapor deposition (CVD) [6], sputtering [9], and MW PECVD [5].

This work reports the synthesis of MWCNT-graphene-like nanocarbon hybrid films directly on nickel substrate without any pretreatment, by using 2.45 GHz, MW PECVD technique. Methane was used as a precursor gas. The as-grown samples were characterized by using Raman spectroscopy, high resolution scanning electron microscope (SEM), high resolution transmission electron microscope (HRTEM), electrical resistance, transmittance and field emission. The effect of deposition pressure on the growth of MWCNT-graphene-like nanocarbon hybrid films and their structural as well as field emission properties were studied.

2. Experimental details

2.1. Direct deposition of MWCNT-graphene-like nanocarbon hybrid films on nickel substrates

MWCNT-graphene-like nanocarbon hybrid films were directly deposited on nickel substrates in a custom designed and developed 2.45 GHz MW PECVD system equipped with the substrate heating facility as shown in Fig. 1. The 2.45 GHz microwave set up consists of 1.2 kW magnetron source, power supply, circulator, three stub tuners and mode convertor. Microwave transmission waveguide setup was attached to the vacuum deposition chamber with the help of a microwave transparent quartz window. The output impedance of mode convertor and input impedance of the deposition cavity was matched by using three stub tuners. High vacuum of the order of 10^{-7} Torr was achieved within the deposition chamber by using a turbo molecular and rotary pump combination. The deposition pressure was controlled and monitored by using a throttle valve and high pressure gauge, respectively. The substrate was heated using molybdenum heating element and the temperature was controlled by the PID controller.

The substrate used for the deposition of carbon structures was a nickel foil of 10 mm square with a thickness of ~250 μm. Nickel foils were first ultrasonicated with isopropyl alcohol (IPA) and acetone for 5 min. The nickel foils were then treated with hot IPA followed by deionized (DI) water. The well cleaned nickel foils were loaded into the deposition chamber and tightly fixed with the heater to attain good thermal contact between the nickel foil and heater. The temperature of the substrate was monitored with the help of a thermocouple connected to the digital display. The samples were heated to 600 °C with the heating rate of ~30 °C/min. A removable sample holder on which the substrates are clamped is placed above the Mo heater. The thermocouple was placed in the heater area but the deposition was started after some time where the temperature of the heater and the substrate equalize. The distance between the heater and the substrate holder is ~2 mm. The temperature was controlled precisely by the PID controller and there is not such difference between the growth temperature and the temperature in the heater area. The nickel foils were pretreated with H_2 plasma for 10 min before the deposition of carbon structures to remove any oxide film formed on the nickel substrate. Argon plasma was first generated using low power. Subsequently, the pressure was increased up to the desired deposition pressure in the range 5–30 Torr using H_2 and CH_4 gas mixtures using a throttle valve. After the H_2 plasma pretreatment, the precursor gases, CH_4, H_2 and Ar were allowed into the chamber to attain certain pressure and adjusted the microwave power to sustain the plasma while depositing the thin film for 5 min. The deposition parameters used for growing MWCNT-graphene-like nanocarbon hybrid films have been summarized in Table 1. After completing 5 min deposition, the gases were turned off and heater was allowed to cool down naturally to room temperature.

2.2. Structural characterization

The morphology and microstructure of the samples were examined by high resolution SEM (JEOL-JSM-7100F) and HRTEM (Tecnai G20, F-30-ST WIN) with field emission electron gun source operated at the electron accelerating voltage of 300 kV. For HRTEM study, the samples were prepared by etching nickel in HNO_3 + HF mixture and collecting the remaining film after diluting the mixture with the DI water on the carbon coated copper grid. The structure and bonding information of the samples were collected by Raman spectroscopy (Renishaw, micro-Raman model in Via Reflex) with 514 nm laser excitation laser using 25 mW/cm^2

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