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Substrate bias induced synthesis of flowered-like bunched carbon nanotube directly on bulk nickel

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A B S T R A C T

This paper reports the effect of substrate bias on the multiwalled carbon nanotube (MWCNT) deposited on nickel foil by microwave plasma enhanced chemical vapor deposition technique. The MWCNTs have been characterized by the scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), Raman spectroscopy, field emission and current–voltage characteristic of the heterojunction diode. The SEM images exhibit unique hierarchical flowered-like bunched and conformally coated MWCNTs. Substrate bias induced ion bombardment helps in the enhancement of hydrocarbon dissociation and is responsible for flowered-like MWCNTs growth. The HRTEM micrographs show the base growth mechanism for MWCNTs. The value of turn on field for emission decreases from 5.5 to 1.9 V/μm and field enhancement factor increases from 927 to 4770, respectively, with the increase of substrate bias. The diode ideality factor of CNT/ n-Si heterojunction is evaluated as 2.4 and the on/off current ratio is found to be 7 at ±2 V, respectively.

1. Introduction

sp^2 bonded carbon is the most stable elementary form of carbon at room temperature and it results into most of the layered carbon allotropes [1]. Graphene, carbon nanotubes and graphite are the layered allotropes of carbon. Carbon nanotubes (CNTs) have emerged as an interesting sp^2 hybridized carbon allotrope owing to their exceptional electrical, optical, mechanical, electrochemical and thermal properties [2–4]. Direct growth of CNTs on the metal bulk substrate provides the advantages of low contact resistance to the substrate, better adhesion and for applications, where a conducting substrate is needed, e.g. supercapacitor, field emitter, fuel cell, etc. The ohmic behavior of the CNTs and the metallic substrate interface which ensures an easy electron transport in spite of this rigidity of CNTs to the substrate, provides the field emitters to withstand high current density during electron emission [5]. The problem of residue catalyst nanoparticle on the tip of CNTs is also solved. In many cases, a diffusion barrier is also used to stop the diffusion of catalyst nanoparticle into the substrate which may enhance contact resistance if any conductive substrate is used. The metallic substrates are superior to the non metallic substrate for CNTs' applications in field emission, battery, supercapacitor, fuel cell, etc. Plasma enhanced chemical vapor deposition (PECVD) induced growth is a well known process for the synthesis of vertically aligned CNTs [6]. In general, an areal density of nanotubes on the conductive substrate such as copper, nickel, etc., is lower because the high surface energy of the metal support hinders catalyst film dewetting and nanoparticle formation [7]. For the cold emitter to be commercialized, it must have low turn on field, high emission current and a good constancy. Low turn on field can be achieved by good ohmic contact between the substrate and the field emitter for easy electron transport while the control of CNTs morphology provides the high emission current. Lahiri et al. [8] have described the factors affecting the stability of field emission current from CNTs such as low barrier between the substrate and CNT to provide uninterrupted electron supply from the substrate, high thermally conductive substrate to extract the heat during field emission due to the contact resistance which may de-bond CNTs from the substrate, presence of gas contaminations which may influence work function and poor vacuum level etc., [8].

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The direct synthesis of CNTs on bulk metal resolves many of these issues. Further, the direct synthesis of CNTs also provides good adhesion to the substrate. Graphene-like sheet structures along with the CNTs also appear simultaneously if the CNTs are grown at high temperature [9,10]. The poor adhesion between the CNTs and the substrate produces short life span of the device [11]. The direct synthesis of dense CNT forests on the metal substrate improves the adhesion which in turn improves the life span of the CNTs based devices. Sugime et al. [12] have used Mo, Co thin film to grow highly dense CNTs on the conductive support. Microwave PECVD is a promising technique [13] to grow carbon nanostructures at low temperature, which are otherwise grown at high temperature by the other techniques [14,15]. Microwave PECVD (MW PECVD) is known to generate low temperature, nonthermal plasma and is capable of the growth of nanostructures, which otherwise cannot be grown without using catalyst [16]. Further, in the MW PECVD, the resulting growth rate is lower due to the unwanted interaction of plasma with the metal [17]. The reflected loss hindered the deposition of building block on the substrate and the reflection loss enhances with the electrical conductivity of the metal substrate [17]. Alignment of CNTs can be obtained by applying negative substrate bias to the substrate during growth. Tsai et al. [18] have studied the effect of both the positive and negative substrate bias on the growth of CNTs. Further, CNTs are known to be promising form of carbon for field emission devices. Kimura et al. [19] have synthesized the flowered structured CNTs on the metal grid with honeycomb structure and achieved low turn on field of 1.09 V/μm. Sridhar et al. [20] have grown CNTs directly on the metal alloy substrate (Inconel), non-metallic Si substrate and proposed their field emission properties in vacuum microelectronics application. Ultra nanocrystalline diamond decorated flowered-like CNTs have used field emitter with the turn on field varying from 1.96 to 2.30 V/μm [21]. Longtin et al. [22] have brazed the CNTs to metal alloy by the active vacuum brazing technique to lower the interfacial electrical resistance of CNTs to the substrate for the enhanced field emission. Recently CNT/Si based heterostructures have found application in the solar cell and photo detector [23–25]. A power conversion efficiency of ~15% has been achieved based on the CNT/Si heterojunction solar cell [23]. Uchino et al. [24] have studied rectifying behavior of CNT/Si (highly doped n-Si with resistivity 0.02 Ω cm) based Schottky diode.

In this paper, we have reported highly dense flowered-like carbon nanotubes deposited by MW PECVD technique on the bulk nickel substrate with the help of negative substrate bias. The multiwalled CNT (MWCNT) have been characterized by the Raman spectroscopy, scanning electron microscopy (SEM), high resolution transmission electron microscopy (HRTEM), field emission and the Schottky heterojunction. The role of negative substrate bias has been studied in the improvement of CNTs density.

2. Experimental

MWCNTs were directly deposited on the nickel substrates by a custom designed and indigenously built MW PECVD system equipped with the substrate heating facility. The MW PECVD system is shown in Fig. 1. The 2.45 GHz microwave set up consists of 1.2 kW magnetron source, power supply, circulator, three stub tuner and mode convertor. A vacuum of the order ~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. Nickel foil with a thickness of ~250 μm was used as the substrate. Nickel foils were cleaned by ultrasonication in isopropyl alcohol (IPA) and acetone for 5 min. After ultrasonication treatment, the nickel foils were treated with the hot IPA followed by the deionized (DI) water. The nickel foils were also treated with H_2 plasma for 10 min before the deposition to remove the native oxide. After the H_2 plasma pretreatment, the precursor gases, CH_4, H_2 and Ar were allowed into the chamber. The flow rates of H_2, Ar and CH_4 gases were kept at 50, 20 and 20 sccm, respectively. The deposition pressure of 20 Torr and the substrate temperature of ~450 °C were used during the growth of CNTs. The samples were deposited without any bias and with different negative substrate biases of −150, −250 and −350 V. The deposition time was 5 min for each sample. The morphology and microstructure of the samples were examined by the scanning electron microscope (JEOL-JSM-7100F). The structural and bonding information of the samples were studied by Raman spectroscopy (Renishaw, micro-Raman model in Via Reflex) with 514 nm laser excitation at the room temperature. The field emission measurements were carried out with a diode configuration using an indigenously developed field emission measurement setup in a vacuum of ~3×10^{-7} Torr. The MWCNT coated nickel substrate was used as the cathode and indium tin oxide (ITO) coated glass was used as an anode. The data were collected using a computer, interfaced with the Keithley 2410 source meter through an IEEE card. The separation between the anode and cathode is defined by the PTFE spacer of thickness ~150 μm and the overlap area between the plate anode and cathode was kept at ~0.196 cm^2.

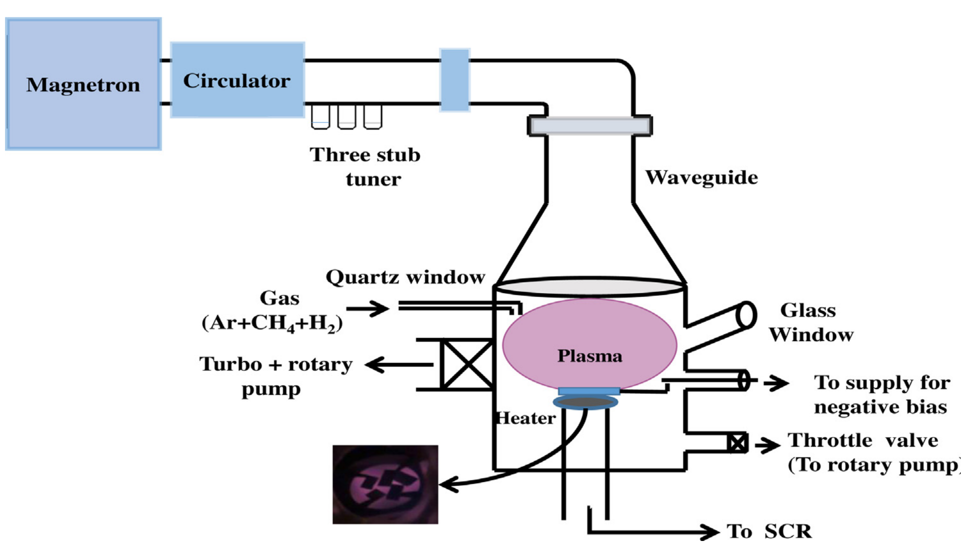

Fig. 1. Schematic of the MW PECVD system.