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Decoration of zinc oxide nanoparticles on vertically aligned single wall carbon nanotubes: An efficient field emitter

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ABSTRACT

In present work, zinc oxide (ZnO) nanoparticles are decorated on the surface of Vertically Aligned-Single Wall Carbon Nanotubes (VA-SWCNTs) to enhance field emission properties of SWCNTs. VA-SWCNTs synthesized by Plasma Enhanced Chemical Vapour Deposition (PECVD) technique are decorated with ZnO nanoparticles by thermal evaporation technique. Modified surface morphologies of as-prepared films were characterized by Atomic Force Microscope (AFM) and Raman spectroscopy to confirm the attachment of ZnO nanoparticles on VA-SWCNTs. Remarkable increase in current density, stability as well as reduction in turn on field were observed in ZnO nanoparticles coated VA-SWCNTs. Attachment of ZnO nanoparticles reduce the turn-on field of VA-SWCNTs field emitters from 2.0 to 1.0 V/μm, while current density increase from 3.6 to 16.8 mA/cm^2 with long term stability and repeatability. The observed results are explained in terms of increased emitting area by modified surface with high field enhancement factor of VA-SWCNTs field emitters.

1. Introduction

Single wall Carbon Nanotubes (SWCNTs) have demonstrated to be an excellent material for field emission application due to their extraordinary properties such as small tip radius, high aspect ratio, high electrical conductivity and good mechanical and chemical stability [1–5]. Due to these amazing properties, SWCNTs have wide applications as electron field emitters in field emission display (FED) [6], X-ray tubes [7] Cathode Ray Oscilloscope and scanning electron microscope [8–13]. Vertically aligned SWCNT instead of randomly oriented SWCNTs, have high electric field enhancement factor (β) which reduces the macroscopic applied field and electric field strength in the vicinity of SWCNTs tip can be enhanced by hundreds of times [14]. Aforementioned points suggested that vertically aligned SWCNTs are highly desirable geometry to be good field emitters [15,16].

In spite of vertically alignedment, reliable commercial electron field emitters based on SWCNTs are still not available due its high degradation rate. Apparently, device lifetime, long-term emission stability and repeatability are the major issues for practical field emission devices that required further improvement of its properties [11–16]. Many techniques have been developed to enhance the stability of SWCNTs for electron field emission [17]. Some attempted to modify the surface of SWCNTs by decoration with suitable metal or metal oxide nanoparticles [18–20]. Metal nanoparticles decorated SWCNTs are becoming the most promising field emitter due to reducing the work function of SWCNTs, consequence of this high current density are occurred at low turn-on field but at the cost of low current stability. Degradation rate of this hybrid nanostructure is high due to low thermal conductivity, low melting point and ion bombardment. To overcome this problem some researchers are decorated SWCNTs by metal oxide nanoparticles such as Go, TiO_2, SnO_2 and ZnO nanoparticles [21–26]. ZnO nanoparticles are the best choice to increase current stability of SWCNTs with amazing and desired FE properties. ZnO is the most important electronic and photonics material owing to its wide direct band gap of 3.3 eV and large exciton binding energy of 60meV [27–29]. On the other hand, ZnO also has been considered to be one of the most promising field emitter due to its negative electron affinity and high chemical stability with high melting point and high thermal conductivity [30,31]. These points suggest that ZnO nanoparticles decorated on vertically aligned SWCNTs

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can be used to make better field emitter compared to either of the other metal oxide nanoparticles. Recent research has demonstrated that ZnO decorated MWCNT/SWCNTs possess excellent field emission properties such as high current density at low turn on field with high chemical and thermal stability [32–34]. However, most of these works were performed on either MWCNTs or non aligned SWCNTs that have the limitation of the low field emission parameters such as low field enhancement factor, low turn-on field with short life [35–38].

To get over these issues, we are presenting a research work on synthesis and enhancing field emission properties of VA-SWCNTs by attachment of ZnO nanopartciles. Plasma enhanced chemical vapour deposition (PECVD) technique is used to synthesise VA-SWCNTs on Si substrate. ZnO nanoparticles are decorated on VA-SWCNTs by thermal evaporation technique.

2. Experimental details

SWCNTs were grown on the n-type Si <100> substrate via Plasma Enhanced Chemical Vapour Deposition (PECVD) technique. Bared Si substrate was ultrasonically cleaned in acetone and dried at room temperature before loading into the RF sputtering chamber for catalyst deposition. Ultrasonically cleaned Si substrate was coated with Fe catalyst at 100 W by RF sputtering technique. The Fe catalyst coated Si substrate was placed upon the graphite heater inside the quartz chamber of PECVD technique. The chamber was then evacuated to 10^{-3} torr and the catalyst film is pre-treated under hydrogen (H_2) atmosphere at a temperature of 600 °C which is measured by a thermocouple directly connected to the graphite heater. Acetylene (C_2H_2) as a source gas at flow rate of 25 sccm was then added for 15 min in continuation with hydrogen (H_2) to start the SWCNTs growth while the heater temperature was quickly raised to 650 °C (growth temperature). During growth process, the pressure inside the chamber was kept at 10 mbar. In this process, dc plasma at a power of 75 W was struck, to assist vertically aligned growth of the SWCNTs. Finally, the growth process was turned off and the sample was then cooled down to room temperature.

The surface morphology of as grown VA-SWCNTs was analysed by field emission scanning electron microscope (FESEM) of FEI (Nova Nano). High resolution transmission electron microscope (HRTEM) was recorded using a Technai G2 F30 S-Twin (FEI; Super Twin lens with $Cs^{1}/_{4}1.2$ mm) instrument operating at an accelerating voltage at 250 kV. The graphitization of as grown SWCNTs was also studied by Raman spectrometer of HORIBA Jobin Yvon (LABRAM HR 800 JY) at a wavelength of 633 nm. The field emission characteristics of the as grown VA-SWCNT sample were carried out in dual electrode arrangement. All the data were recorded at room temperature in a high vacuum chamber. The current density and field enhancement factor were calculated using JE plot and Fowler Nordheim (FN) plots respectively.

Further, ZnO nanoparticles were synthesized and decorated on VA-SWCNTs by thermal evaporation technique. In this technique, ZnO nanopartciles were formed by vaporizing the Zn powder in presence of oxygen. As-grown VA-SWCNT sample was placed on the sample holder inside the vaccum chamber of thermal evaporation system. Pure Zn (99.9%) powder was loaded on the tungsten boat and fitted it in vaccum chamber as source material. The process starts in high vaccum. To achieve this vaccum, chamber was evacuated of the order of 10^{-5} Torr by using rotary and diffusion pump. At the level of this vaccum, the heating of Zn was initiated by passing the current to vaporise the Zn powder. At the same time, the oxygen gas was passed into chamber at pressure 0.1 Torr for the growth of ZnO nanoparticles. Oxygen pressure was maintained throughout the evaporation. After this, switch off the system and allowed to cool. Sample was taken out from the vaccum chamber of thermal evaporation technique.

The decorated VA-SWCNTs sample was subjected to all the above characterization techniques like FESEM, HRTEM, AFM and Raman spectroscopy for confirmation of decoration of ZnO nanoparticles. To understand the influence of decoration of these ZnO nanoparticles on field emission behaviour, we performed a detail comparison of field emission study of VA-SWCNT and ZnO/VA-SWCNTs. Field emission parameters, such as turn-on field, current density, emission current stability, field enhancement factor and repeatability of these samples are reported. These obtained results are correlated with their micro and nanostructure revealed by FESEM, HRTEM, AFM and Raman spectroscopy.

3. Results and discussions

3.1. FESEM characterization

SEM is used to analyse the surface morphology of VA-SWCNTs and also examined to confirmation of decoration of ZnO nanopartciles on VA-SWCNTs. In Fig. 1(a), SEM image of VA-SWCNTs grown by PECVD technique on silicon substrate is depicted. It is clear from this SEM micrograph that high density of VA-SWCNTs has been successfully synthesized. Diameter of VA-SWCNTs is found to be approximately ~1–2 nm. ZnO nanoparticles decorated VA-SWCNTS can be clearly seen in Fig. 1(b). SEM image reveals that ZnO nanoparticles in sphere form are successfully decorated on

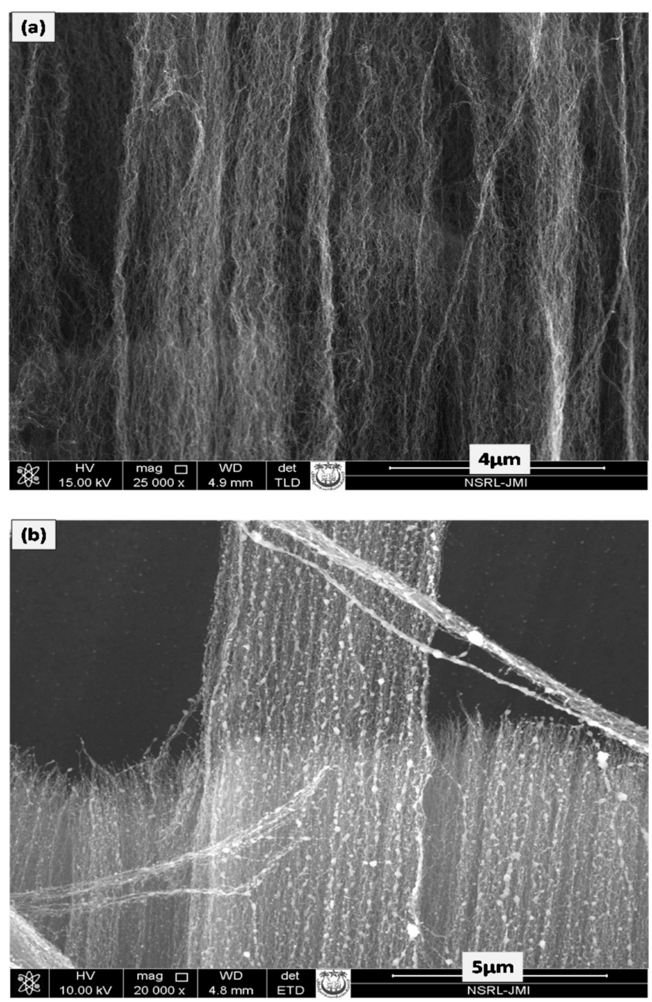

Fig. 1. FESEM images of (a) as-grown VA-SWCNTs by PECVD technique (b) ZnO nanoparticles decorated VA-SWCNTs.