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Improved field emission from indium decorated multi-walled carbon nanotubes

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ABSTRACT

Multi-walled carbon nanotube (MWCNT) films were grown using thermal chemical vapor deposition (T-CVD) process and were decorated with indium metal particles by thermal evaporation technique. The In metal particles are found to get oxidized. The In decorated films show 250% enhancement in the FE current density, lower turn-on and threshold fields, and better temporal stability as compared to their undecorated counterpart. This improvement in field emission properties is primarily attributed to increased density of states near the Fermi level. The presence of O 2p states along with a small contribution from In 5s states results in the enhancement of density of states in the vicinity of the Fermi level.

1. Introduction

Starting from the landmark discovery of the carbon nanotubes (CNTs) [1], significant applications have been found of CNTs in various fields. Due to their outstanding properties, like high aspect ratio [2], good electrical [3] and thermal properties [4], high mechanical stiffness [5], and chemical inertness [6], they are used in field emission (FE) electron sources [7,8], nano-electronics [9], energy applications [10], hydrogen storage [11], sensors [12] etc. CNT based FE electron sources have been employed in different applications like field emission displays (FEDs) [13], FE electron microscopes [14], miniature X-ray tubes [15], and microwave amplifiers in satellite communication [16]. Low turn-on and threshold fields, high current density and maximum temporal stability are important features of a FE source for device applications. Several methods have been reported for enhancing the FE properties of CNTs like growth of CNT arrays on patterned substrate, pattern transfer process to reduce the screening effect [17,18], coating or decoration of low work function nanoparticles on the CNT tips to reduce the width of the tunneling barrier and increase the number of emission sites [19], introducing an interlayer between CNTs and substrate for better growth, adhesion and reduced contact resistance [20], doping of CNTs with different metal particles for increasing field enhancement factor and emission sites density [21]. There are reports pertaining to decoration of CNTs with various low work function materials in the nanoparticle form such as Cs, LaB_6, Hf, BaSrO, $SrTiO_3$, CeB_6, Ta etc. Also, some wide band gap materials like SiO_2 and MgO were deposited using different coating techniques like sputtering, spin coating, thermal evaporation, and pulsed laser deposition (PLD) [22–29]. Enhanced field emission from CNTs after plasma treatment [30], low energy ion bombardment [31], high temperature annealing [32], electrical treatment [33] and CNT carpet were also reported [34]. It is mentioned theoretically that these coatings change the electronic structure of CNTs top surface and thus increase the density of states near the Fermi level [35]. These two parameters, low work function and increased number of states near the Fermi level with high aspect ratio enhance the FE properties. There is a report on improved FE properties of In_2O_3/SWCNT composite film prepared by a chemical bath deposition [36] where a maximum current density (J_{Max}) of 3.5 mA/cm^2 at 7 V/μm was reported. To the best of our knowledge, this is the first report to investigate the FE properties of indium decorated MWCNT films and achieved improved FE properties including enhancement in maximum current density (J_{Max}) and long-term temporal stability.

In the present work, lower work function metal In ($\Phi = 4.1$ eV) is decorated on CVD grown MWCNTs by thermal evaporation technique. FE measurements reveal that In decorated films show 250%

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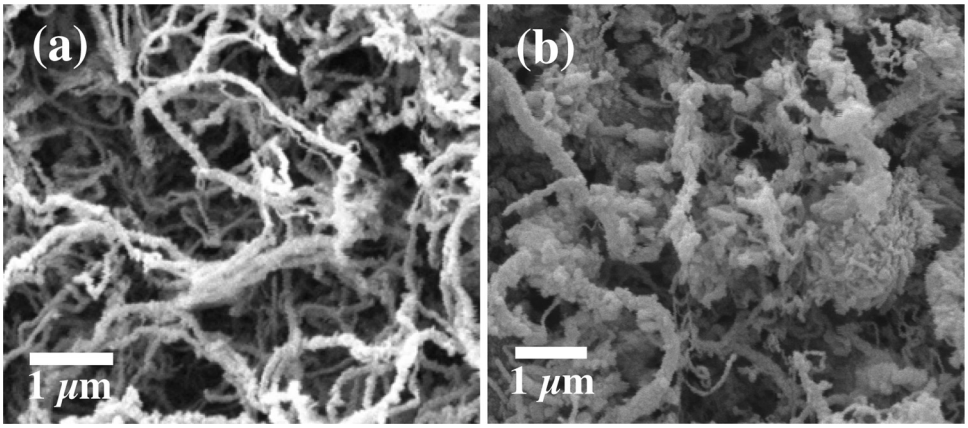

Fig. 1. SEM images of (a) pristine CNT and (b) In(50 nm)/CNT films. In coating is clearly visible in the second case from the image contrast.

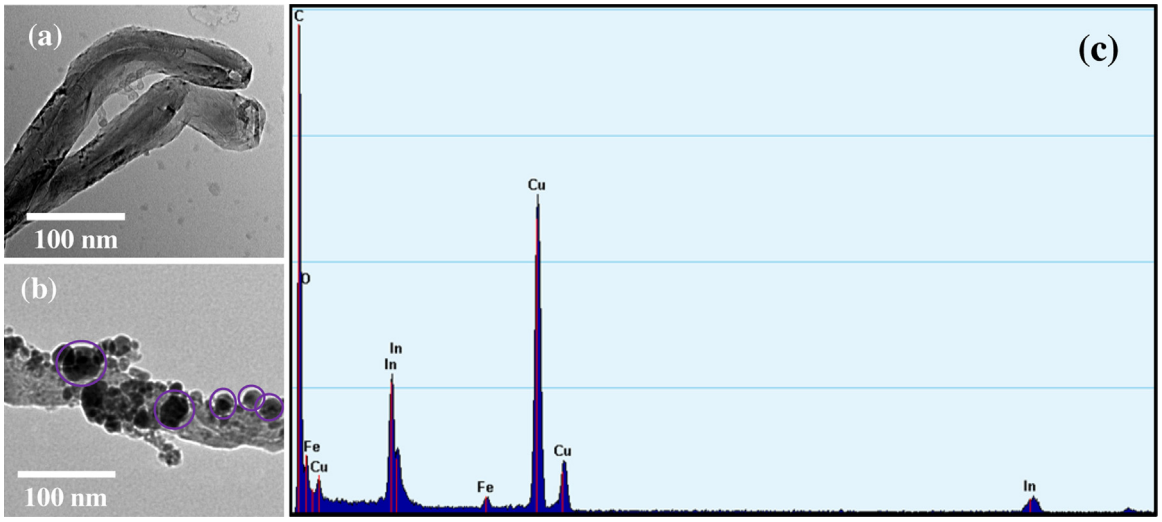

Fig. 2. TEM images of (a) pristine CNT and (b) In(50 nm)/CNT films, In metal particles (encircled) are clearly visible in the second case and is confirmed from (c) spot EDX from the encircled regions indicating presence of In.

enhancement in the FE current density ($\sim J_{Max}$), lower turn-on (E_{ON}) and threshold fields (E_{TH}), and better temporal stability as compared to their undecorated counterpart. This is primarily attributed to increased density of states near the Fermi level as observed by X-ray photoelectron spectroscopy (XPS). The other factors which could also contribute to enhance the FE in In decorated films are improvement in-plane graphitic crystallinity and slight enhancement in electron emission sites. The In decoration on tip and walls of CNTs are seen by high resolution transmission electron microscope (HRTEM). Thickness of the coated layers and diffusion of In in CNTs are examined using Rutherford backscattering spectroscopy (RBS).

2. Experimental

MWCNTs were grown using a thermal chemical vapor deposition technique (T-CVD) in double zone furnace configuration. Liquid precursor xylene used for carbon source and ferrocene powder used for catalytic source. Firstly, homogeneous solution (0.02 gm/ml) of ferrocene and xylene was prepared. The prepared solution was used for CNT growth on the silicon substrate at 730 °C in the higher zone with solution vaporizing temperature of 450 °C in the lower zone as reported earlier [37]. The grown CNT films were coated with In metal of two different thicknesses (50 nm, 100 nm) using a thermal evaporation technique at a base pressure of 5×10^{-5} mbar. The In coating thickness was determined using quartz crystal oscillator fitted in thermal evaporation set up and subsequently confirmed by Stylus profilometer. It has also been calculated by fitting the RBS with 2 MeV He^{+2} and found to be 62 nm (±6 nm) and 125 nm (±12 nm) for In(50 nm)/CNT film and In(100 nm)/CNT films respectively. The morphology and microstructure of the films have been examined by scanning electron microscope (SEM: ZEISS EVO 50) and HRTEM (JEM2100F). Energy dispersive X-ray spectroscopy (EDX: Model-Swift ED3000) attached with SEM, was used for elemental identification. Structural analysis of the films is studied by Raman spectrometer (RENISHAW in Via Raman Microscope). XPS measurements, using Mg Kα source (1253.6 eV) were performed in ultra high vacuum ($\leq 10^{-9}$ torr). The Kelvin probe (KP) measurements were performed to determine the work function of the films.

Electron FE measurements were performed using an indigenously developed FE set up. CNT films were used as cathode, circular steel plate was used as an anode, and anode-cathode distance was fixed at 300 μm using a stepper motor, having precession control of about 5 μm. The FE chamber was evacuated up to the base pressure of 1×10^{-7} mbar with a rotary pump and a turbo molecular pump connected in series. An electric field was applied between electrodes using high voltage DC power supply (Stanford Model: PS350) and corresponding FE current readings were measured using an Electrometer (Keithley 2000 DMM) which are connected