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Microscopy Studies of Carbon Nanotubes / Ferroelectric Composites for Microelectronics

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Top-down approaches for continuous scaling-down of devices and components in semiconductor industries is getting increasingly difficult and expensive, and thus bottom–up strategies, e.g., growth of functional nano-structures using nanowires or nanotubes are being explored rather than patterning and etching [1]. Carbon nanotubes (CNTs) are an interesting option under consideration due to their extraordinary physical and electrical properties [2] that make them suitable for microelectronic applications, such as, semiconductor field-effect-transistors (FET) and capacitors. In recent years, the fabrication of one-dimension (1D) ferroelectric (FE) nanostructures have been investigated as a capacitor for future 3D memories, however several difficulties need to be overcome in particular fabrication and characterization [3]. In this work, the fabrication of ferroelectrics (FE) (e.g., $Pb_{1-x}Zr_xTiO_3$ (PZT) and $BaTiO_3$ (BT)) multi-walled carbon nanotubes (MWCNTs) composites were synthesised by chemical solution deposition (CSD) method, namely sol gel. Later, the composites were investigated using scanning electron microscope (SEM) equipped with energy dispersive spectroscopy facilities and transmission electron microscopy (TEM) in addition to X Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR), to address the compatibility between FE and CNTs.

CNTs tend to agglomerate due to high van der walls forces. To overcome week forces and to have good dispersion for the electrophoretic deposition (EPD) on the top of the substrate, the tubes were purified and functionalized: purified with hydrochloric acid (HCl) followed by functionalization with nitric acid (HNO_3) and sulphuric acid (H_2SO_4). The MWCNTs used in this work have diameters ranging from 15-35 nm and length up to 4 µm (Figure 1(a)). FTIR spectrum depicts the broad adsorption band at 3438 cm^{-1} which is attributed to hydroxyl groups (OH^-). The stretching of C=C, O-H bending deformation in -COOH and CO bond stretching in the functionalized-MWCNTs are observed at 1635 cm^{-1}, 1436 cm^{-1}, and 1073 cm^{-1} respectively, indicating that carboxyl and hydroxyl functional groups were attached to the surface of MWCNTs (Figure 1(b)). The functionalized groups improve the wettability of MWCNT, which was estimated by the contact angle measurements; as low the contact angle is, as high the wettability (Figure 1(c)). MWCNTs mats were obtained by EPD on $Si/SiO_2/TiO_2/Pt$ substrates in aqueous media. Mats of MWCNTs were coated with PZT and BT and heat treated in air and reducing atmospheres. Figure 1(d) depicts the TEM micrograph of MWCNTs coated with PZT sols after drying at 120 ºC for 24 h, clearly showing the coverage of the MWCNTs with the ferroelectric. XRD patterns depicted in Figure 2 attest the phase purity of MWCNT/FE composite after annealing. For MWCNTs/BT composites annealed in air and N_2 a perovskite single phase was formed, whereas in case of MWCNTs/PZT annealed in N_2, additional peaks appear that need further investigation. The phase formation of the ferroelectric oxides was further confirmed by SEM / EDS (Figure 3). PZT coated MWCNT have a diameter of approximately 80 nm and EDS depicts the presence of Pb, Zr and Ti elements, which proves the efficacy of the coating. Similarly, BT/MWCNTs composites illustrated in Figure 4, have a diameter of approximately 100 nm and the EDS spectra confirmed the BT coating of MWCNT.

Thus purified and functionalized MWCNT/FE composites were successfully fabricated by sol gel. After annealing at 550 °C – 700 °C crystalline MWCNTs/PZT and MWCNTs/BT composites were obtained, respectively.

References

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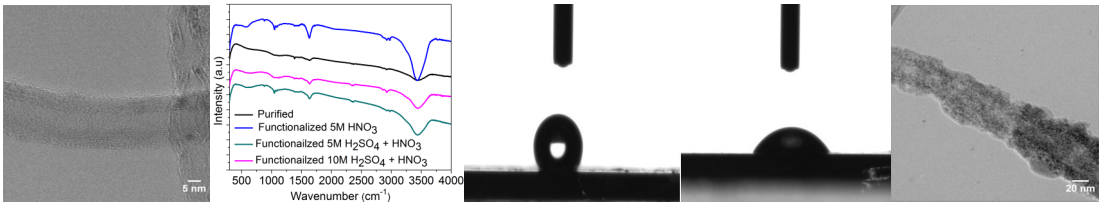
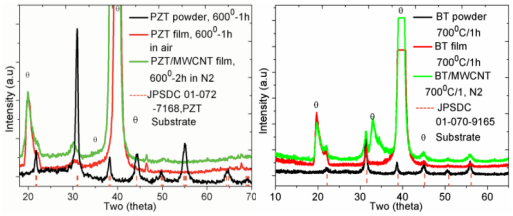
2. Mauricio Terrones *et al.*, Annual Review of Materials Research 33: 419-501, 2003
3. S. Kawasaki *et al.*, Applied Physics Letters 92, 053109, 2008



(a) (b) (c) (d)

Figure 1. (a) TEM micrograph of purified MWCNT; the diameter of ~ 20 nm, (b) FTIR spectra of purified and functionalized MWCNTs and (c) Contact angle measurements with water (left) for purified (high contact angle) and (right) functionalized (low contact angle) MWCNT films deposited by EPD (d) TEM micrograph of MWCNTs coated with PZT sol, dried at 120 ºC for 24 h.

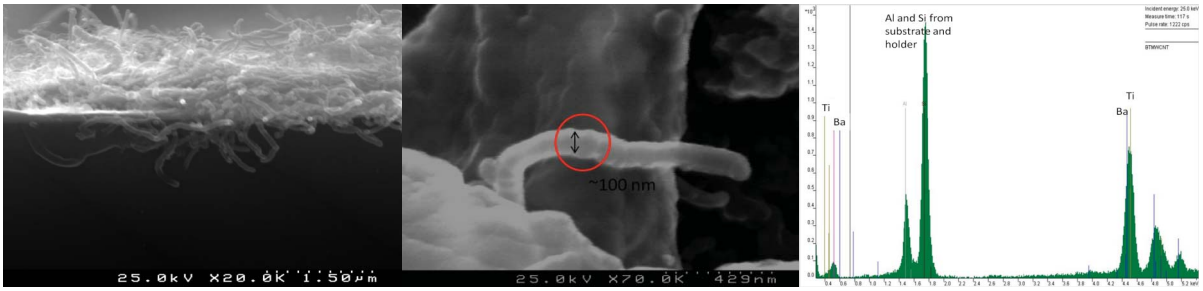


(a) (b)

Figure 2. X-ray diffraction patterns of (a) PZT powders and films heat treated in air and PZT/MWCNT heat treated in N2 atm. and (b) BT powders and films heat treated in air and BT/MWCNT heat treated in N2 atm.

(a) (b) (c)

Figure 3. SEM micrographs of MWCNT/PZT composites after annealing at 600 ºC in nitrogen: (a) film cross section, (b) magnified view of a single tube coated with PZT and (c) EDS on a coated tube.



(a) (b) (c)

Figure 4. SEM micrographs of MWCNT/BT composites after annealing at 700 ºC in nitrogen: (a) film cross section, (b) magnified view of a single tube coated with BT and (c) EDS on a coated tube.

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