ZnO Functionalization of Multi-walled Carbon Nanotubes for Methane Sensing at Single PPM Concentration Levels

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Bare carbon nanotubes (CNTs) are insensitive towards most target gases due to poor bonding between the chemically inert graphitic surface and different compounds they are exposed to. For practical applications, the functionalization of CNTs is required and, by introducing surface pre-treatments, their efficiency is enhanced making it possible to produce highly sensitive CNT chemiresistor-based sensors.

Due to the energetically favorable electron transport in ZnO-MWCNT junctions[1], compared with previously reported Pd-MWCNT[2], we have applied ZnO as the functionalizing material for surface pre-treated multi-walled CNTs (MWCNTs). ZnO was deposited on O_2 plasma and UV O_3 pre-treated MWCNTs using diethylzinc as the precursor (Arradiance Gemstar ALD tool at 175/200/225^{0}C). The green laser Raman spectroscopy of the ZnO-MWCNT shows that the D, G′, G band peaks of the CNTs are preserved, while additional Raman peaks originating from the ZnO layer appeared (Fig. 1). Furthermore, as the ALD process temperature was increased, the ZnO peaks became stronger, suggesting that ZnO deposited on top of the MWCNTs at higher temperatures during the ALD process improves the crystalline quality of the devices. This result was confirmed by energy-dispersive x-ray spectroscopy (EDS) using a scanning electron microscope (SEM) (Fig. 2).

The sensor response ($(R_{methane}-R_{air})/R_{air} = \Delta R/R_{air}$) was measured inside a test chamber where CH_4 in air calibration mixtures were introduced as the concentration was continuously monitored using a reference CH_4 detector (Fig. 3). Our novel ZnO-MWCNT methane sensor is capable of detecting a 2 ppm concentration of methane in air at room temperature, the best reported sensitivity for CNT-based methane sensors to this date.

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[1] H. Zhang , N. Du , B. Chen , D. Li, & D. Yang, *Science of Advanced Materials* 2009 , *1*(1), 13-17.
[2] Y. Lu , J. Li, J. Han, H. T. Ng , C. Binder, C. Partridge, & M. Meyyappan, *Chemical Physics Letters* 2004, *391*(4), 344-348.
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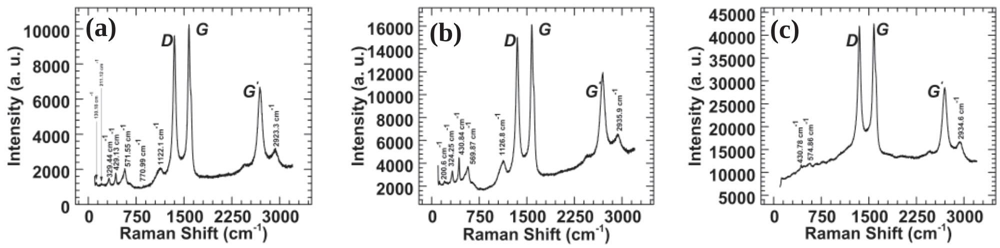

Figure 1: Raman spectra obtained from the ZnO-MWCNT samples after ALD at (a) 225 ^{0}C, (b) 200 ^{0}C and (c) 175 ^{0}C. The peaks at 200.6 cm^{-1}, 429.13 cm^{-1}, 572.2 cm^{-1} and 329.44 cm^{-1} correspond to $2E_2^{low}$, E_2^{high}, A_1 (LO), E_2^{high} - E_2^{low} modes of ZnO, respectively, thus suggesting samples with good crystalline quality.

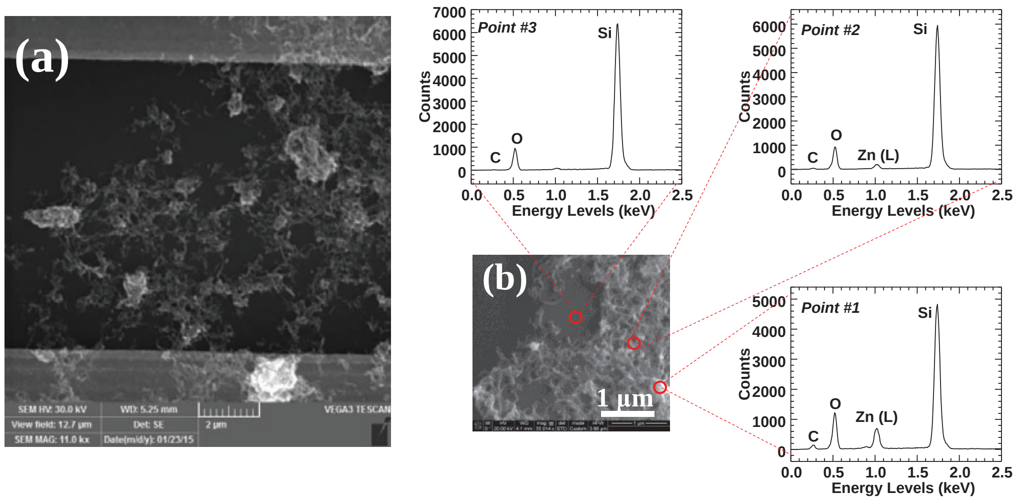

Figure 2: (a) SEM image of MWCNTs confined between two Au electrodes. (b) SEM and EDS results obtained from a UV-O_3 treated ZnO functionalized MWCNT sample fabricated by ALD at 225 ^{0}C. The Zn (L-Line) peak was only found on the MWCNTs (stronger on brighter point 1, weaker on less brighter point 2). Point 3, which is on the SiO_2 substrate, did not show a Zn signal.

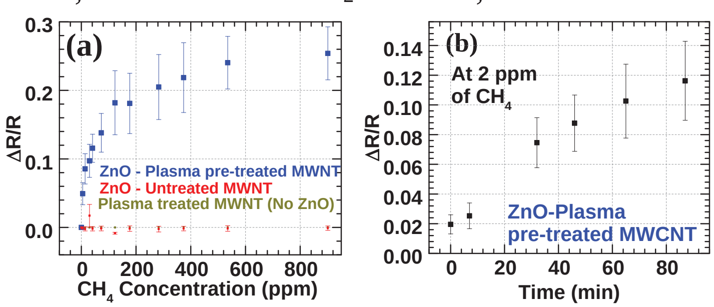

Figure 3: (a) Room temperature sensor response (ΔR/R) for ZnO- plasma pre-treated MWCNT, ZnO-untreated MWCNT and plasma treated but not ZnO functionalized MWCNT sensor. (b) Time dependence of the sensor response when exposed to a CH_4 concentration of 2 ppm.

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