Microsensors based on multi-wall decorated carbon nanotubes and few-layer graphene

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Nanoscale graphitic carbon materials like carbon nanotubes (CNT) and, more recently, few-layer graphite (graphene) have attracted much interest due to unique combination of electrical, mechanical, chemical properties and many potential applications. However, for successful applications of these materials in microdevices like gas sensors, reliable and compatible technologies of controlled synthesis or deposition, manipulation, functionalization, decoration, integration and others, comprising specific technological platforms, should be developed.

In this work, multi-wall carbon nanotubes and few-layer graphene have been utilized to fabricate gas sensors with extremely low power consumption. The technologies of processing and manipulation have been established first for multi-wall carbon nanotubes. To provide selective sensitivity to different gases, the nanotubes were decorated by various metal or metal oxide (Ti, Sn, Ni, TiO_2, SnO_2, CePrOx, etc.) nanoparticles (NP) using several chemical or physical processes. Then, decorated nanotubes were deposited from liquid solutions precisely over pairs of metal (Ti, W, Au) electrodes with micron scale gaps using ac di-electrophoresis, to form a chemical resistor configuration, Fig. 1. After deposition, thermal annealing in vacuum was used for electrical contact improvement. Both suspended and supported (over SiO_2 substrate) nanotubes were tested. To obtain suspended nanotubes, FIB milling was used to make deep trenches between electrodes, before nanotubes deposition.

The samples (CNT/NP) were characterized using various microscopy techniques (SEM, TEM, EDX, EELS, confocal Raman, Raman imaging, AFM). Electrical measurements were carried out to evaluate performance of CNT/NP based sensors in the presence of various gases (Ar, N_2, O_2, H_2S) in a gas chamber. Two different effects during CNT/NP-gas interaction were observed: i) electrothermal (change of the nanotube resistances due to their cooling by gas, as nanotubes can be heated up strongly in vacuum by current - Joule effect), ii) chemical interaction between nanoparticles and the injected gas. The characteristic times differ very strongly for these two processes, that helps to distinguish between their contributions. The Joule effect (self-heating) was found to heat up suspended nanotubes up to 300-400 C at applied biases as low as 0.5 V (microwatt power consumption), while much smaller heating was observed for supported CNTs, due to unexpectedly high heat dissipation to the SiO_2 substrate.

On the other hand, self-heating of nanotubes by current was found to increase dramatically the reactivity of nanoparticles towards reactive gases. In particular, this effect allowed to obtain high sensitivity in detection of oxygen by Ti decorated nanotubes at *room temperature*, which is impossible for conventional thin film sensors, Fig. 2. For comparison, with supported nanotubes, measurable signals were obtained only when substrate was heated to 150-200 C.

Similar technologies have been applied here also to fabricate few-layer graphene (FLG) based gas sensors. These sensors can have some advantages over CNT base ones, for example much bigger area can be exposed to gases, resulting in increased sensitivity. Utilizing an ac di-electrophoresis method, we were able to deposit FLG in suspended or supported configurations, Fig. 3. Some samples were studied using confocal Raman spectroscopy to study spatial distribution of the FLG flake properties (not shown). The annealing performed in a high vacuum (< $5x10^{-6}$ Torr) at 850 ^oC, was found to dramatically reduce electrical resistance down to a few hundreds of kΩ. Preliminary results of tests carried out with gases like O_2 and propanol vapor and Sn-decorated FLG have shown the possibility of using such devices as highly-sensitive gas or pressure sensors in a suspended chemi-resistor configuration, see Fig. 3.

References

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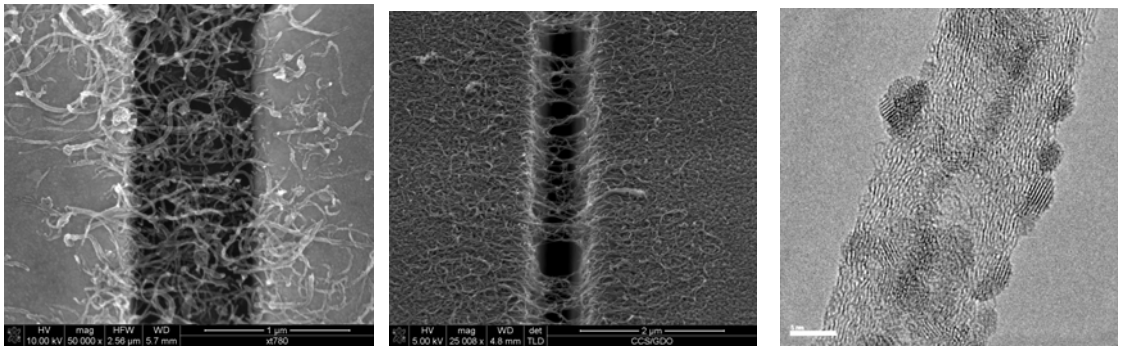

Fig. 1. SEM images of multi-wall carbon nanotubes in supported (left) or suspended (center) sensor configuration, and TEM image of SnO_2 decorated nanotube (right)..

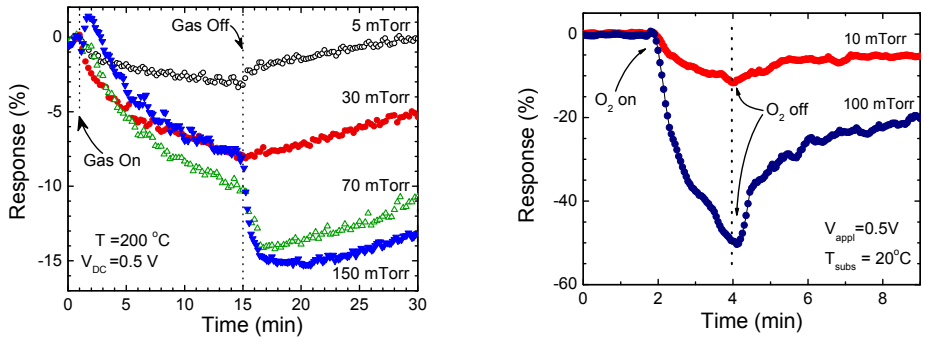

Fig. 2. Sensor response for O_2 pulses in the vacuum chamber for Ti-decorated multi-wall carbon nanotubes in supported (left) or suspended (right) sensor configuration.

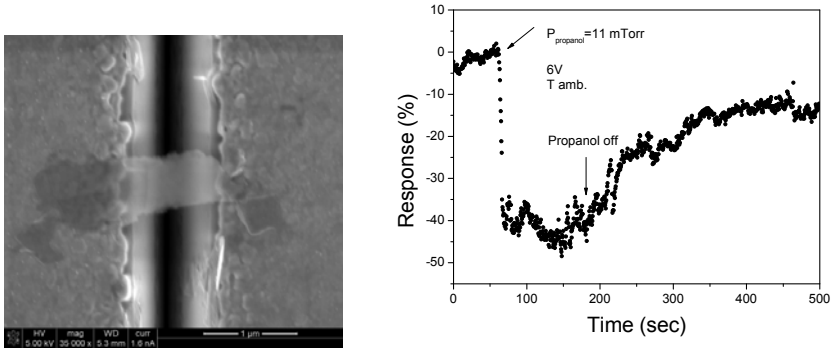

Fig. 3. Suspended FLG flake deposited over electrodes (left) and sensor response for Sn-decorated FLG when propanol vapor is injected in the vacuum chamber.