Plasma Functionalization of Multi-Walled Carbon Nanotubes for Ammonia Gas Sensors [†]

Alexander G. Bannov [1],[*] and Anton Manakhov [2],[3]

[1] Novosibirsk State Technical University, 20 K. Marx, Novosibirsk 630073, Russia

[2] Research Institute of Clinical and Experimental Lymphology–Branch of the ICG SB RAS, 2 Timakova str., Novosibirsk 630060, Russia

[3] RG Plasma Technologies, Central European Institute of Technology—CEITEC, Masaryk University, Kamenice 5, Brno 625 00, Czech Republic

[*] Correspondence: bannov@corp.nstu.ru

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Abstract: The role of plasma functionalization of multi-walled carbon nanotubes (MWCNTs) for room temperature ammonia gas sensors was investigated. Plasma functionalization of MWCNTs with maleic anhydride was carried out with various durations. Active material of gas sensor was investigated by scanning electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. It has been shown that formation of functional groups on the surface of carbon nanotubes led to the increase in ammonia sensor response by 2–4 times. The increase of functionalization duration induces the rise of O:C from 0.28 to 0.335, increase of sensor resistance, and the distortion of shape of I-V curves.

Keywords: carbon nanotubes; functionalization; plasma; gas sensor; ammonia; response; plasma treatment; functional groups

1. Introduction

Carbon nanotubes (CNTs) are of interest within last decades and the research on their synthesis, modification, and applications are still carried out all over the world. Multi-walled carbon nanotubes (MWCNTs) is a promising material for various applications due to their lower cost, simplicity of synthesis and scale-up compared to single-walled carbon nanotubes. MWCNTs can be used in polymer composites [1,2], hydrogen evolution reactions [3,4], electronics [5], biosensors [6], etc.

In addition, CNTs can be used as active material for gas sensors [7–9]. Recently, the research on room temperature gas sensors based on CNTs for ammonia detection is of particular interest [10–12]. However, the response of gas sensors based on untreated CNTs is low enough. Therefore, there are several approaches to enhance the sensing properties, such as the use of conducting polymers [13], plasma treatment [14,15], deposition of metallic [16] and oxide [10,17] nanoparticles. Plasma functionalization makes it possible to significantly improve capturing of ammonia molecules on the surface of carbon nanotubes. In [18] the oxygen plasma was used for modification of multi-walled carbon nanotubes, the sensitivity of modified gas sensors towards ammonia was twice higher than that of untreated sensing material. Treatment of MWCNTs in oxygen plasma and plasma co-polymerization of maleic anhydride (MA) and acetylene [19] led to the formation of core-shell structures with relatively high response (22.5% towards 100 ppm NH_3). Kim et al. [15] created ammonia gas sensor based on O_2 functionalized MWCNT/PANI sensor reaching the response $3.34\%/(ppm\ NH_3)$ within a range 10–100 ppm NH_3.

In this paper, the effect of duration of plasma functionalization of MWCNTs using co-polymerization of maleic anhydride and acetylene for ammonia gas sensor was investigated. This approach makes it possible to enhance the sensor response of MWCNTs to NH_3 by means of increase of concentration of surface functional groups.

2. Methods

MWCNTs were deposited on Si/SiO_2 substrate by plasma enhanced chemical vapour deposition (PECVD). The growth of CNTs was carried out on iron catalytic nanoparticles. The nanoparticles were deposited in microwave plasma torch with dual-flow nozzle electrode according to the technique described in [20,21]. Si/SiO_2 substrate was placed in a holder for 4 samples with 4×4 mm deposition area for each sample. The argon was used as a carrier gas. The flow rates of argon through the central and outer channels were 700 and 28 sccm, respectively. The outer channel was used to fed the $Fe(CO)_5$ vapours. This compound forms Fe nanoparticles as a result of decomposition. The deposition of nanoparticles was carried out for 15 s with plasma power of 210 W. The iron nanoparticles on the Si/SiO_2 substrate were placed into tubular furnace where the decomposition of acetylene was performed at 600 °C. Firstly, the samples were reduced in Ar (1400 sccm)/H_2 (500 sccm) mixture for 10 min, then the flow was switched to Ar (1400 sccm)/C_2H_2 (25 sccm) and the deposition of CNTs was carried out for 10 min. Subsequently, the active layer of sensors was covered by gold contacts (325 nm layer, 6.65 mm × 2.33 mm) with 25-nm thick NiCr interlayer.

MWCNT sensors was plasma treated in MA-C_2H_2 plasma using the equipment described in [21,22]. Briefly, the sensor with sealed Au contacts was placed into special holder.The deposition of plasma polymer was carried out by dielectric barrier discharge (DBD) plasma co-polymerization of MA and C_2H_2. The discharge was ignited between planar metallic electrodes covered by Al_2O_3 ceramics, 1-mm thick, on the bottom of which the sensor was placed. The gases were supplied by a 1 mm slit between the high voltage electrodes. The vapors of MA were fed into the discharge by means of Ar flow (Messer, 99.998%) purging throw the MA pellets (Sigma-Aldrich, 99%). The flow rate of the second monomer, C_2H_2 (Messer, 99.6%) was set to 2 sccm. The Ar flow rate through the bubbler was 0.5 slm. The total Ar flow rate was kept at the level of 1.5 slm. The deposition was carried out in the discharge ignited by 5.4 kHz sinusoidal high voltage. The power supplied by the generator was 20 W. Three samples of gas sensors with various durations of deposition (2 min, 5 min, and 7 min) were obtained.

The gas sensor was characterized by means of measuring the resistance of sensor under ammonia exposure. The measurements were performed using a custom made setup with two gas channels: synthetic air (Linde) and the analyte (NH_3 diluted in air). The scheme of the setup was described in [23] in detail. The sensor was placed into the measuring chamber on the heater, operated by an Agilent U3606A DC power supply (Agilent). The resistance of active layer of sensor was measured by the two point technique between the gold electrodes using Keithley 2410 Source Meter (Keithley). A fixed bias voltage 1 V was applied. The sensor response was calculated as

$$\frac{\Delta R}{R_0} = \frac{R - R_0}{R_0} \tag{2}$$

where R and R_0 are the resistances of sensors in a mixture synthetic air/NH_3 and in a pure synthetic air, respectively. The concentration of ammonia was varied from 100 ppm to 500 ppm. All samples were tested at the same conditions, room temperature (25 ± 2 °C) and relative humidity 2–2.5%.

Current-voltage (I-V) characteristics of the sensors were measured by 4200-SCS Semiconductor characterization system (Keithley) within a range from −5 V to +5 V at room temperature (25 °C). Morphology of the CNT sensing material was determined by scanning electron microscopy (SEM) using Tescan MIRA (TESCAN) equipped with electron-dispersive X-ray spectroscopy add-on. Disorder degree of CNTs was determined by Raman spectroscopy using Renishaw spectrometer (Renishaw) in a range of −100–3200 cm^{-1} ($\lambda = 514$ nm). X-ray photoelectron spectroscopy (XPS) was used to analyze the chemical composition of surface layers using EA125 spectrometer fitted on

custom built UHV system. The measurements were used at pass energy of 25 eV and power 270 W. To excite XPS spectra Al Kα radiation (1486.6 eV) was used.

3. Results and Discussion

SEM images of the functionalized MWCNTs used as active material of ammonia gas sensor are presented in Figure 1. As it can be seen, the morphology of carbon nanotubes remains almost unchanged after plasma functionalization with maleic anhydride because of low duration of treatment and relatively mild conditions. The samples of MWCNTs deposited directly on Si/SiO$_2$ substrate were represented by strongly entangled carbon nanotubes with large number of walls. The sample also contained small fraction of cup-stacked carbon nanofibers.
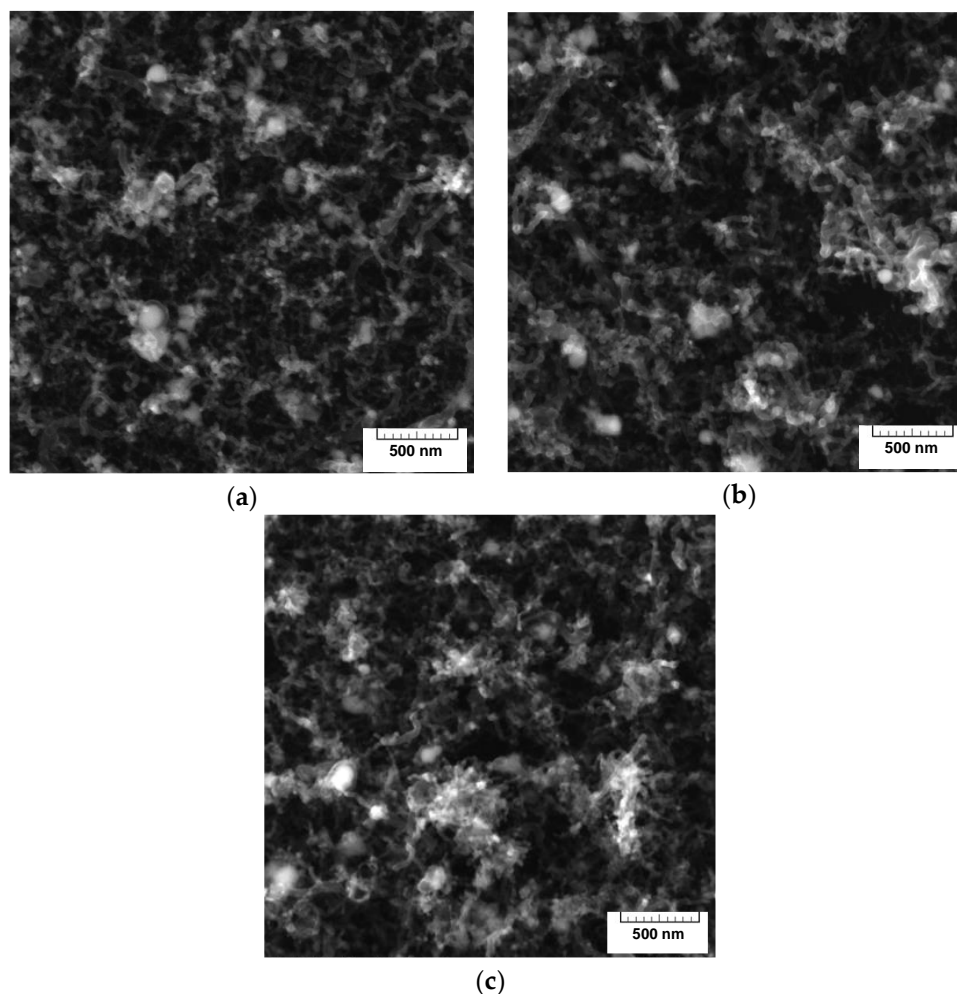

(**a**)

(**b**)

(**c**)

Figure 1. SEM images of MWCNTs before and after functionalization at various durations: (**a**) 2 min, (**b**) 5 min, (**c**) 7 min

Raman spectra of plasma treated MWCNTs are shown in Figure 2a. The spectra of plasma functionalized MWCNTs consist of two bands typical for carbon nanomaterials, D mode (1353 cm^{-1}) which can be attributed to disorder structure and G mode (1589–1592 cm^{-1}) relating to graphitic structure of the material [24,25]. The ratio of intensity of these two modes indicates the disorder degree of the material. Plasma treatment leads to the increase of I(D)/I(G) (Table 1) indicating the decrease of contribution of C-C bonds in the form of sp^2 hybridization. It can be noted that any treatment of MWCNTs can produce a lot of defects on its surface, but the results on I(D)/I(G) confirm relatively mild conditions of plasma functionalization compared to other types of treatment, such as chemical functionalization reported in [26].
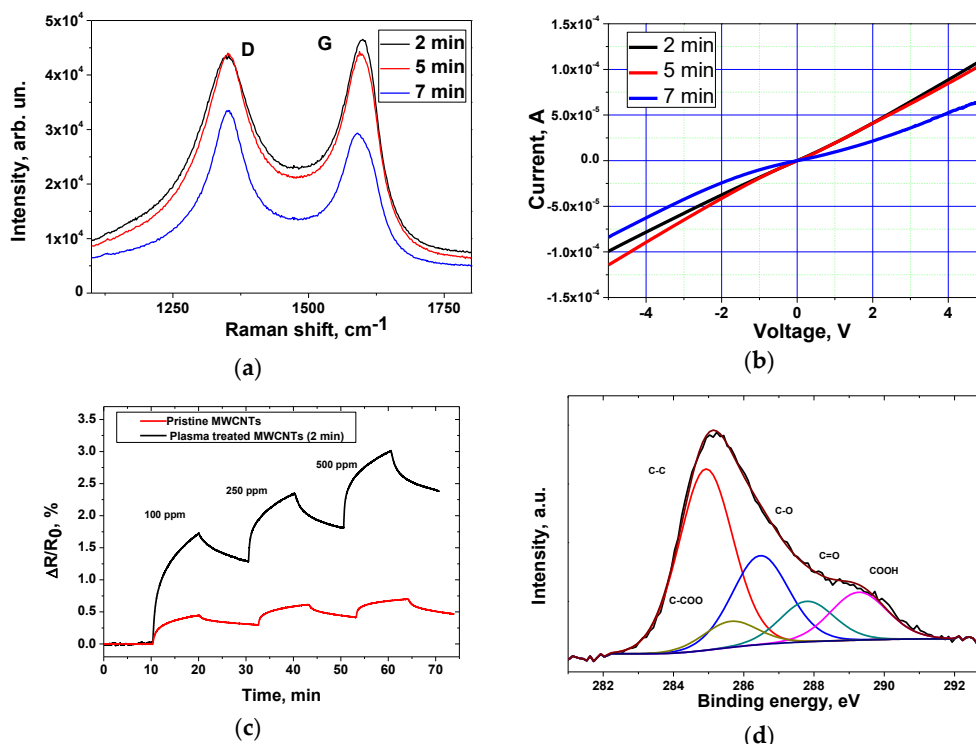
(a)

(b)

(c)

(d)

Figure 2. (**a**) Raman spectra of samples obtained using various durations of plasma treatment; (**b**) I-V curves of active layer of gas sensor; (**c**) Typical response curve of pristine MWCNTs and MWCNTs plasma treated for 2 min; (**d**) XPS spectrum of MWCNT sample plasma treated for 2 min.

Table 1. Parameters of Raman spectra of plasma treated MWCNTs.

Sample	D Peak Position, cm^{-1}	D Peak FWHM, cm^{-1}	G Peak Position, cm^{-1}	G Peak FWHM, cm^{-1}	I(D)/I(G)
2 min	1353	130	1591	65	0.87
5min	1353	119	1592	70	0.95
7 min	1353	90	1589	59	1.08

I-V curves of the active layer of ammonia gas sensors are presented in Figure 2b. Current-voltage (I-V) characteristic of sensor treated during 2 min was almost linear that corresponds to conductive material. Increasing of the treatment time led to appearance of non-linearity of the I-V curve due to change of conduction mechanism to semiconducting because of functional coating formed on the carbon surface.

Sensor responses are shown in Table 2.

Table 2. Response of gas sensors before and after functionalization of MWCNT active layer.

Duration of Treatment	Resistance of Sensor, kΩ	Sensor Response before Functionalization, %			Sensor Response after Functionalization, %		
		100 ppm	250 ppm	500 ppm	100 ppm	250 ppm	500 ppm
2 min	52.7				1.7	2.3	2.9
5min	58.6	0.4	0.6	0.7	1.8	2.6	3.6
7 min	110				0.7	1.0	1.3

The resistance of sensors grows when increasing the duration of treatment due to the formation of plasma coating on the surface of MWCNTs. The resistance of initial non-treated MWCNTs was

only 18 kΩ, and the plasma treatment led to the increase of resistance to 52.7–110 kΩ. This fact is caused by the formation of relatively thin film of plasma polymer on the surface of MWCNTs.

Typical curves of sensor response are shown in Figure 2c. The response of gas sensors was within a range 0.3–0.6% for 100–500 ppm NH_3. Plasma treatment led to the growth of sensor response to 1.7–2.9% (2 min). The maximum response was observed at 5 min of treatment and further growth of duration of treatment led to the decrease of response to 0.7–1.3% (100–500 ppm). This is in agreement with O/C determined by XPS which was 0.28, 0.35, and 0.335 for 2 min, 5 min, and 7 min, respectively. Typical XPS spectrum of the sample treated for 2 min is presented in Figure 2d. The data show that the increase of duration of treatment above some level (5 min) led to the formation of lower concentration of surface oxygen-containing functional groups.

4. Conclusions

The presented results show that plasma functionalization of MWCNTs can be effective in the enhancement of ammonia detection using the room temperature gas sensors. Plasma functionalization made it possible to increase the sensor response towards ammonia by 3–4 times compared to pristine MWCNTs. The increase of duration of plasma functionalization induces the rise of O:C from 0.28 to 0.335, the increase of sensor resistance, and the distortion of shape of I-V curves.

Conflicts of Interest: The authors declare no conflict of interest.

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