Chapter 12
Room Temperature Hydrogen Sensor Based on Pt/TiO_2/MWCNT Composites

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Abstract Pt-doped TiO_2/MWCNT composites have been prepared by the sol–gel route and tested in resistive devices for the low temperature monitoring of hydrogen. A morphological and microstructural investigation by SEM, TEM, XRD and micro-Raman spectroscopy of the composites was carried out. Results indicated that, regardless the nominal C/Ti molar ratio, only the anatase phase of titania is formed. Thin films of the Pt-doped composites, deposited on interdigitated ceramic substrates, showed promising hydrogen sensing at low temperatures. On the basis of the results obtained, some hypotheses on the sensing mechanisms operating on these nanostructured hybrid materials have been formulated.

12.1 Introduction

Hydrogen-based systems truly promise a futuristic energy scenario, where hydrogen fuel will be used in fuel cells for civil transportation and in rockets for space vehicles. All these applications necessitate the development of hydrogen sensor devices, which allow its safe and controlled use [1].

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G. Neri et al. (eds.), *Sensors and Microsystems*,
Lecture Notes in Electrical Engineering 91, DOI: 10.1007/978-94-007-1324-6_12,

Numerous metal oxide thin films work at high temperature in air as effective resistive hydrogen sensors, allowing detection of this gas down to very low concentration. However, many of these devices need ambient oxygen to operate, and moreover they fail to detect hydrogen at high concentrations due to saturation effects.

Then, there is also great interest in detecting high concentrations of hydrogen in reducing or inert atmosphere, by means of devices operating at temperature as low as possible, preferably room temperature. In this paper, preliminary data are reported obtained employing a Pt/TiO_2/MWCNT composite as sensing layer for monitoring high concentrations of hydrogen in inert atmosphere at near room temperature.

12.2 Experimental

Pt/TiO_2/MWCNT composites were prepared as follows. First, TiO_2/MWCNT was synthesized by a sol–gel method starting from a mixture of MWCNTs, previously functionalised by a nitric acid treatment at 110°C for 18 h, dispersed in a solution of titanium isopropoxide in isopropanol. A detailed characterization by XRD, SEM, TEM and micro-Raman spectroscopy was carried out. Sensing tests were carried out in an apparatus, interfaced with a PC, composed by a stainless steel box, where is allocated the sensor, and connected to gas supply (He and H_2) and a power supply that allows fixing and controlling the working temperature (in the range 25–100°C), and measuring the resistance values of the sensor when it is maintained under H_2/He mixtures flow (100 ml/min) by means of a resistance meter. The sensor response is defined as $[(R–R_0)/R_0] \cdot 100$, where R_0 is the resistance recorded under He and R the resistance recorded under H_2/He mixture. Before carrying out the sensing measurements, sensors were pre-treated "in situ" upon different experimental conditions.

12.3 Results and Discussion

12.3.1 Microstructural Investigation

TiO_2/MWCNT composite samples with nominal C/Ti molar ratio ranging from 3.6 to 17.0 were first synthesized. The typical morphology of the resulting composite materials is reported in the SEM and TEM micrographs of Fig. 12.1, showing the titania particles dispersed in the mats of carbon nanotubes.

XRD analysis showed only the presence of the diffraction peaks of crystalline anatase. This agrees with micro-Raman analysis carried out on the same samples. Indeed, regardless the C/Ti molar ratio, four main spectral features are clearly

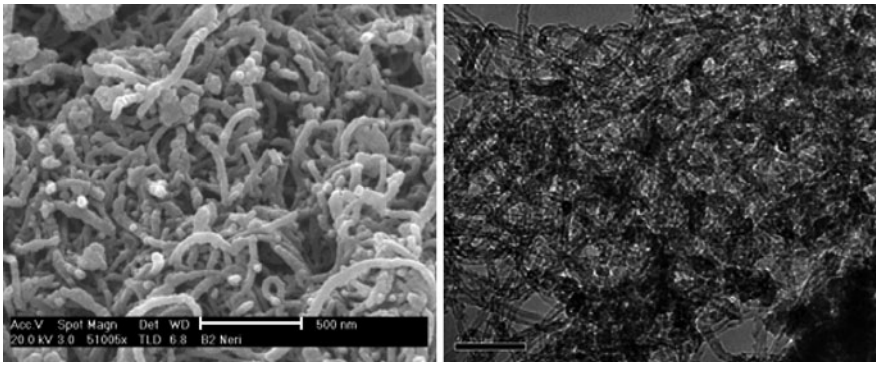

Fig. 12.1 SEM and TEM micrographs showing the morphology of the TiO_2/MWCNT composite materials

visible in the spectra of TiO_2/MWCNTs, centred approximately at 150, 395, 515 and 635 cm^{-1}. The comparison with frequency positions and relative intensities of titania reference-spectra evidences a marked similarity with the spectrum of anatase [2]. Therefore, it is concluded that, even if the presence of smaller amounts of rutile and/or brookite cannot in principle ruled out, anatase is the phase mainly present in the titania nano-clusters of the TiO_2/MWCNT hybrid composites.

Subsequently, 2 wt% of Pt was introduced by the wetness impregnation method, using a solution of platinum acetylacetonate in acetone. The resulting Pt/TiO_2/MWCNT composites were treated at 200°C for 2 h in a mixture of 5% H_2 in argon. Micro-Raman spectra of the ternary composites do not differ from those reported for the corresponding TiO_2/MWCNT composites.

12.3.2 Hydrogen Sensing Tests

Preliminary data have shown that the behaviour of the composite sensors is, as expected, strongly related to Pt presence, working temperature and "in situ" pre-treatment under reducing conditions.

Moreover, the sensor response is strongly affected by the C/Ti ratio; preliminary tests indicated that the best sensing performance is obtained for C/Ti = 3.6.

Figure 12.2 shows the resistance variations registered for the Pt/TiO_2/MWCNT (C/Ti = 3.6) composite-based sensor, after different "in situ" reducing treatments. It can be seen that the reducing treatment has a positive effect on the sensor performance. Specifically, the "in situ" pre-treatment is useful to obtain a better stability of the baseline. Moreover, a decrease of the baseline resistance and an enhancement of the sensor response were registered.

The comparison of the response of the Pt/TiO_2/MWCNT sensor, with that of binary sensors, is reported in Fig. 12.3. It can be clearly seen that hydrogen

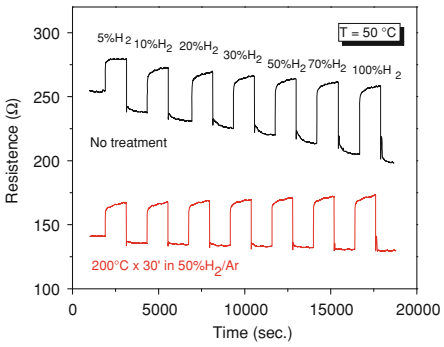

Fig. 12.2 Response to different H_2 concentrations of the Pt/TiO_2/MWCNT sensor (C/Ti = 3.6) after various "in situ" reducing treatments

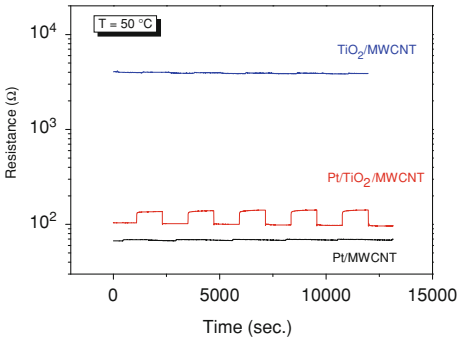

Fig. 12.3 Response to hydrogen of sensors investigated based on different compositions

monitoring takes place only with the Pt/TiO_2/MWCNT ternary sensor, suggesting a synergic action among metal oxide, noble metal and carbon nanotubes.

12.3.3 Hydrogen Sensing Mechanism

A detailed investigation of these materials to better understand the hydrogen sensing mechanism is actually in progress. However, on the basis of the preliminary data so far obtained, some hypotheses can be formulated. Starting from the observation that the sensor measurements were conducted in inert atmosphere without oxygen, the usual mechanism involving the removal of chemisorbed oxygen by hydrogen cannot be invoked. It is likely that the hydrogen molecules get adsorbed at the defects on the titania surface. Then, the sensor response can be attributed to a "spill-over" mechanism, in which chemisorbed hydrogen molecules, are dissociated by platinum, and finally spill out of the Pt, diffusing into the TiO_2 surface layer. This agrees with the fact that both platinum and TiO_2 are necessary to obtain the sensor response. MWCNTs act providing a preferential pathway to the current flow and a larger specific surface area for the adsorption of

hydrogen molecules. According to current view, once the active hydrogen atom is chemically adsorbed at the interstitial positions in the oxide lattice structure, partial electron charge transfer occurs to the *n*-type TiO_2 and the conductance should increases [3]. Vice versa, we observed that the sensor resistance increases in hydrogen. In literature this has been explained suggesting a *p*-type behavior of the metal oxide [4], or a H → TiO_2/MWCNT charge transfer which reduces the hole concentration in the carbon nanotube structure, increasing the resistivity in the system [5]. In order to get a deeper insight into the sensing mechanism a more systematic investigation was planned, aimed at clarifying the role of MWCNTs-TiO_2 interaction. Further investigations are also planned aiming to optimise the formulation of the sensing layer devoted to the development of a prototypal device.

12.4 Conclusion

Pt-doped TiO_2/MWCNT composites have been synthesized by a sol–gel approach, characterized and tested as sensing layer in resistive devices. Results of characterization studies have revealed that, regardless the nominal C/Ti molar ratio, only the anatase phase of titania is formed. Their sensing behaviour towards near room temperature monitoring of hydrogen was strongly related to C/Ti ratio, working temperature and "in situ" pre-treatment under reducing conditions. The results reported seem to be promising in view of obtaining inexpensive high concentration hydrogen-sensors.

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