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# Sensitivity to Reducing Gases of Polymer-Iron Nanocomposite Materials

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**Abstract.** Electrical properties of new Polymer-Iron nanocomposite materials obtained by laser pyrolysis were investigated, in order to find applications for the detection of reducing gases. The aim of this paper was to prove the necessity of complex experimental investigation in order to point out the contribution of different types of adsorption. Usually resistance measurement cannot fully describe the surface interactions. The electron affinity changes are of real interest for in-field conditions which always involve humidity of surrounding gas-atmosphere. On the other hand, the nanocomposite materials can be a solution for specific gas-sensing properties.

## 1. Introduction

Selective detection of different noxes potentially present in the surrounding atmosphere is of real interest for many researchers and users.

Chemical sensors based on different metal oxide semiconductors have been reported for their special gas-sensing properties [1–5]. One of the most important problems of in-field applications is the relative humidity depending on atmospheric conditions.

A possible solution could be the nanocomposites, due to their specific electrical properties resulting by the association of two different materials.

In the present paper a special attention was focused on Fe/$Fe_2O_3$/polyoxocarbosilane core shell nanocomposite. The nanocomposites (Fe-based nano cores enveloped with polymeric polyoxocarbosilane shells) were prepared by the IR laser co-pyrolysis of iron pentacarbonyl and hexamethyldisiloxane. The nanocomposite layer was deposited on Alumina substrate provided with platinum electrodes and a back-side platinum heater. Depending on the temperature provided by the heater, the iron-based cores become superficially oxidized in atmosphere [6] and a steady-state value of the electrical resistance can be measured. The reducing gases (carbon monoxide and methane) react with the preadsobed oxygen or $OH^-$ groups; therefore the electrical resistance is related to free electrons concentration changes. All these surface interactions take place in atmospheres with specific relative humidity, and we focused our experimental investigations on pointing out the role of this environmental parameter.

## 2. Experimental

### 2. 1. Preparation

The black nanosized composites possessing iron-based cores embedded in polyoxocarbosilane layers were produced in a flow reactor, by the IR laser pyrolysis of gas-phase reactants, as described in details elsewhere [7]. The employed precursors were iron pentacarbonyl vapours and hexamethyldisiloxane. The focused continuous-wave $CO_2$ laser radiation (200 W maximum output power, $\lambda = 10.6$ µm) orthogonally crossed the gas flows emerging through three concentric nozzles. $Fe(CO)_5$ vapours (about 25 Torr vapour pressure at 20°C) entrained by a flow of 60 sccm $C_2H_4$was admitted through the central inner tube, while HMDSO vapours entered in the reaction cell through an intermediate, middle tube. The carrier gas for HMDSO was $C_2H_4$ (10 sccm). The reactive gas flow was confined to the flow axis by a coaxial Ar stream (the third, outer tube). Since both $Fe(CO)_5$ and HMDSO do not absorb in the 10.6 µm region, $C_2H_4$ was used as sensitizer (it is excited by the absorption of the $CO_2$ laser radiation and transfers, by collision the absorbed energy towards the other reaction partners thus finally increasing the translation temperature of the whole system). During the experiment, the pressure in the reactor was maintained constant (450 mbar).

For performing sensing tests upon the nanocomposite sample, this was heated in air at 500°C (for stabilization). For resistance measurements, the nanopowder was deposited on Alumina substrates provided with Platinum electrodes and back-side Platinum heater, which ensures the temperature of the active layer.

### 2. 2. Characterisation

TEM images of the nanoparticles are presented in Fig. 1a. The particles in the polymer cages present mostly spherical shapes which coexist with rather elongated dark cores.

By heating the sample at 500°C, structural changes appear (Fig. 1b). The darkish outer shell seems much thinner, loosing its “fluffy”, polymer-like appearance. The particles if not agglomerated exhibit individual mono crystal appearance and a slight growth related to the non heated samples [8, 9].

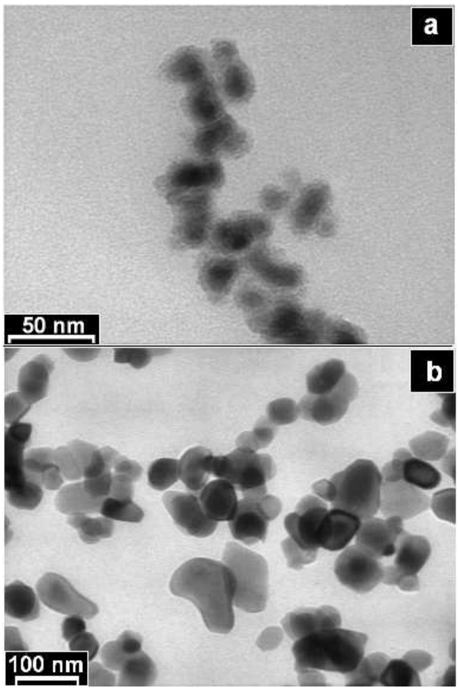

**Fig. 1.** TEM images of the nanocomposites.

Electrical properties changes due to the chemical surface interaction were investigated by a complex experimental setup (Fig. 2) for simultaneous measurement of resistance and CPD.

The experimental system consists in a Gas Mixing Station, a digital Keithley 2000 multimeter and a McAllister Kelvin Probe [10] which is basically a vibrating capacitor with an oscillating reference plate while the other being the surface of the sensor.

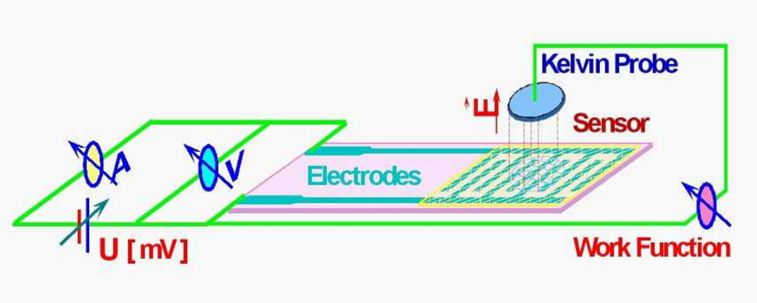

**Fig. 2.** Setup for simultaneous measurement of resistance and relative work function.

The Gas Mixing Station ensures the environmental gas conditions in a dynamic computer controlled way. The digital Keithley 2000 multimeter (DMM) measures the electrical resistance (Fig. 3).

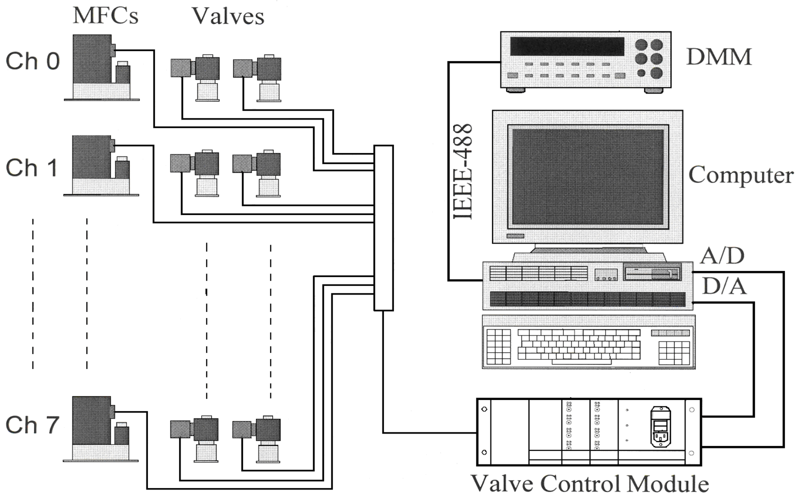

**Fig. 3.** Gas Mixing Station Component parts and electrical connections.

The Kelvin Probe (Fig. 4) measures the contact potential differences (CPD) between different gas atmosphere compositions.

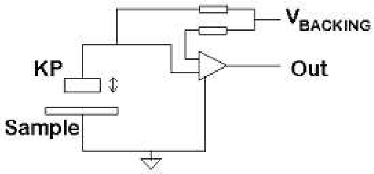

**Fig. 4.** Setup for Kelvin Probe measurements.

It is known from the theory of adsorption that the surface coverage is usually proportional to work function changes due to adsorption.

The work function Φ contains three contributions: the energy difference between Fermi level and conduction band in the bulk $(E_C - E_F)_{bulk}$, the band bending $qV_S$ and the electronic affinity $\chi$. All three contributions may change upon gas exposure.

Simultaneous evaluation of these two physical parameters will permit the calculation of the electron affinity changes [11].

$$CPD * e = \Phi = (E_C - E_F)_{bulk} + qV_S + \chi$$

$$G = G_0 \exp\left\{\frac{(E_F - E_C)_{bulk} - qV_S}{k_B T}\right\}$$

$$G = G_0 \exp\left\{\frac{(\chi - \Phi)}{k_B T}\right\}$$

$$\Delta\Phi = \Phi_F - \Phi_I = k_B T \ln({}^{G_I}\!/_{G_F}) + \chi_F - \chi_I$$

$$\Delta CPD * e = \Delta\Phi = k_B T \ln({}^{R_F}\!/_{R_I}) + \Delta\chi$$

## 3. Results

In order to find gas-sensing applications, the relative humidity cannot be neglected; therefore the experimental investigations have been done in humid synthetic air (30% RH).

$CH_4$ and CO were both investigated because of in-field application (CO can be present as a product of the incomplete burning of $CH_4$). On the other hand, the selectivity of the active layer is an important task for gas-sensing applications.

Usually resistance measurement (Fig. 5) shows that Polymer-Iron nanocomposite material is stable in reference air (the line of reference resistance), sensitive to methane and selective relatively to carbon monoxide.

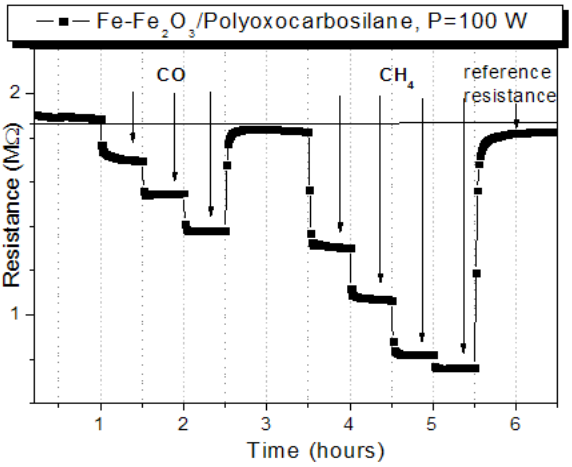

**Fig. 5.** Electrical resistance evolution for $T_{\text{measure}} = 600°C$, RH = 30%, CO = 100, 250, 500 ppm; $CH_4$ = 500, 1000, 2500, 3200 ppm.

A deep insight analyse reveals that the sensitivity to both gases isn't to high (max 1.3 for CO and 2.5 for $CH_4$).

In order to explain the low sensitivity, one problem needs to be explained, respectively in which way the adsorption takes place: chemisorptions or physisorption. The first one modify the charge carrier concentration (band bending $qV_S$), as time as the second can be seen only through the influence of electron affinity changes $\chi$. The temperature of the layer is the parameter that induces changes of the adsorption ration.

By assuming a grain boundary sensing model, the reaction with the gas molecules at the nanocomposite surface yields to a change in the inter-grain potential barrier height. Therefore, the principle operation of semiconductor gas sensors consists of surface potential barrier variation due to adsorption / desorption processes [11, 12]. Adsorption of the atmospheric gases takes place on the surface of $Fe/Fe_2O_3$/polyoxocarbosilane, grain boundaries playing an important role in the sensing model.

From experimental point of view, electrical resistance and CPD were measured simultaneously for different concentrations of each reducing gas, at different temperatures, in humid air conditions. $\Phi$ and $\chi$ were calculated and represented for CO (Figs. 6–8) and $CH_4$ (Figs. 9–11).

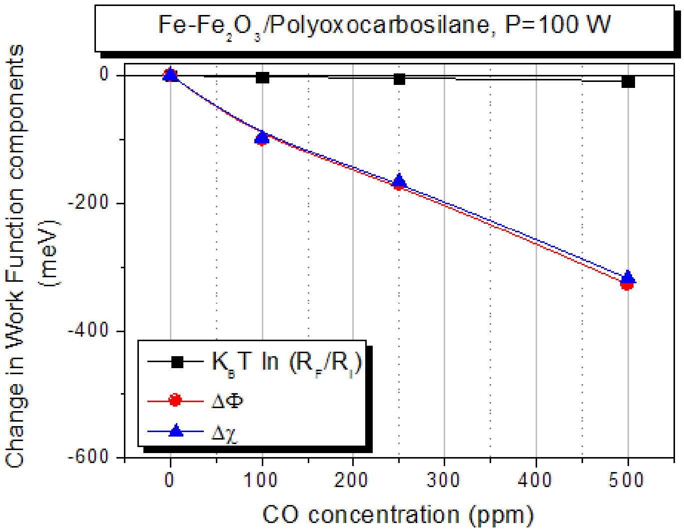

**Fig. 6.** Work Function components for 0–500 ppm CO
RH = 30%, $T_{measure}$ = 300°C.

As general observation, in the case of CO, $\chi$ strongly decreases with the concentration increasing. We consider that the surface interaction between preadsorbed water vapours and CO is the dominant process as time as the Iron particles are in the polymer cages.

It may consist in chemical interaction between CO and $OH^-$ groups with carrier concentration changes ($k_B T \ln R_F/R_I$) changes), but in principal in physical interactions which affect the surface dipoles orientation ($\Delta\chi$ changes). With the temperature increase, the water vapours desorption is faster than CO adsorption and the role of each process is affected (Fig. 8).

In the case of $CH_4$, the relative variation of physical parameters is quantitatively different. The increase of temperature of the sensing layer determines higher variation of all tree components. This can be due the high activation energy needed for methane dissociation.

On the other hand, work function changes $\Delta\Phi$ are in principal determined by electronic affinity changes $\Delta\chi$, band bending $qV_S$ being a secondary effect of methane interaction.

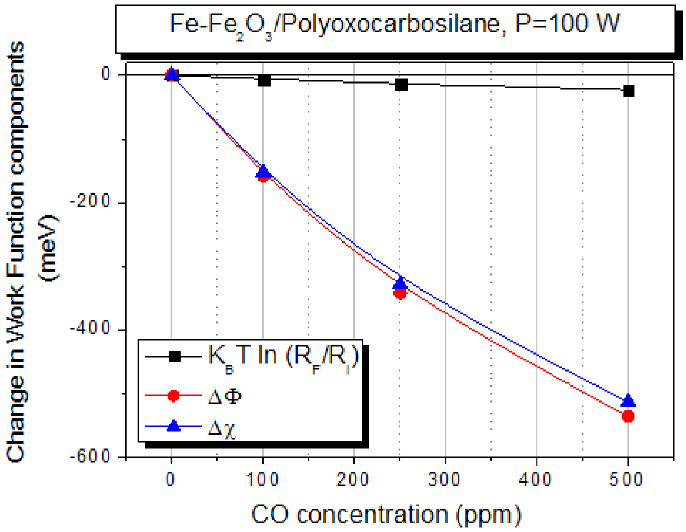

**Fig. 7.** Work Function components for 0–500 ppm CO; RH = 30%, $T_{measure}$ = 450°C.

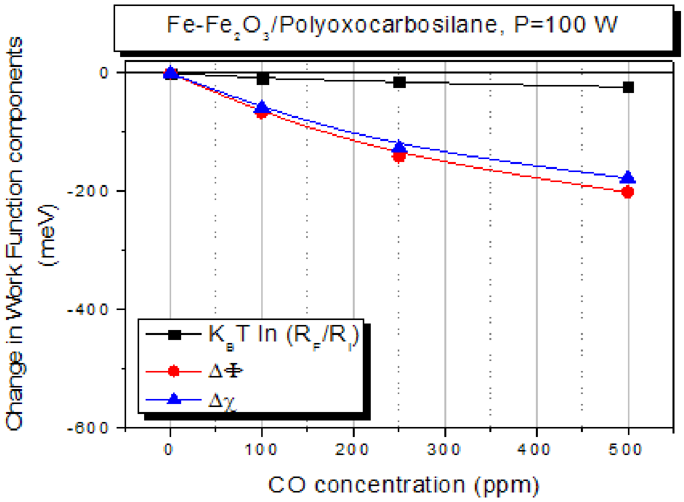

**Fig. 8.** Work Function components for 0–500 ppm CO; RH = 30%, $T_{measure}$ = 600°C.

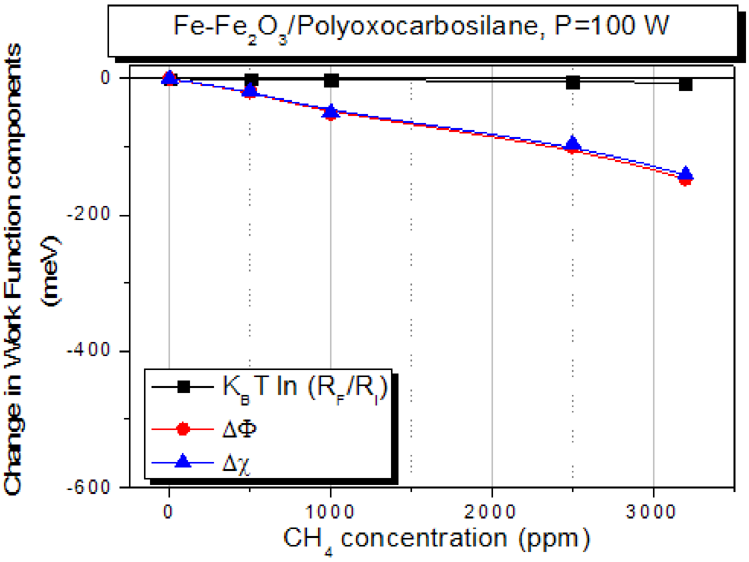

**Fig. 9.** Work Function components for 0–3200 ppm $CH_4$;
RH = 30%, $T_{measure}$ = 300°C.

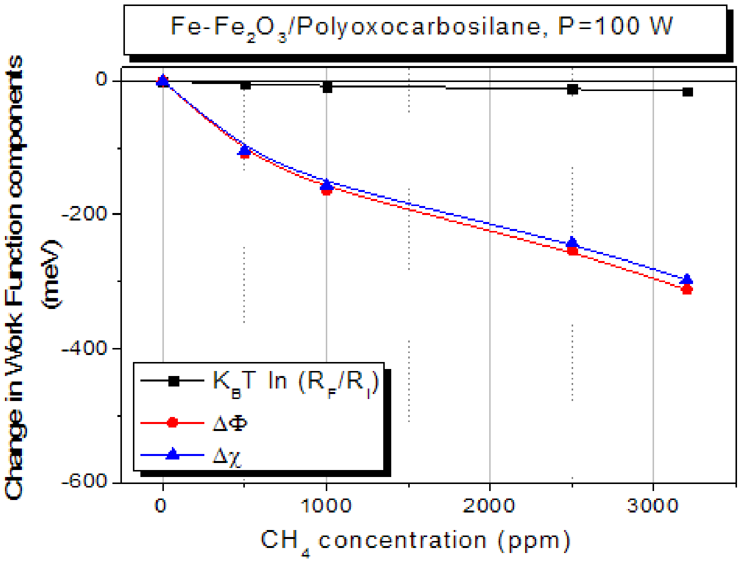

**Fig. 10.** Work Function components for 0–3200 ppm $CH_4$;
RH = 30%, $T_{measure}$ = 450°C.

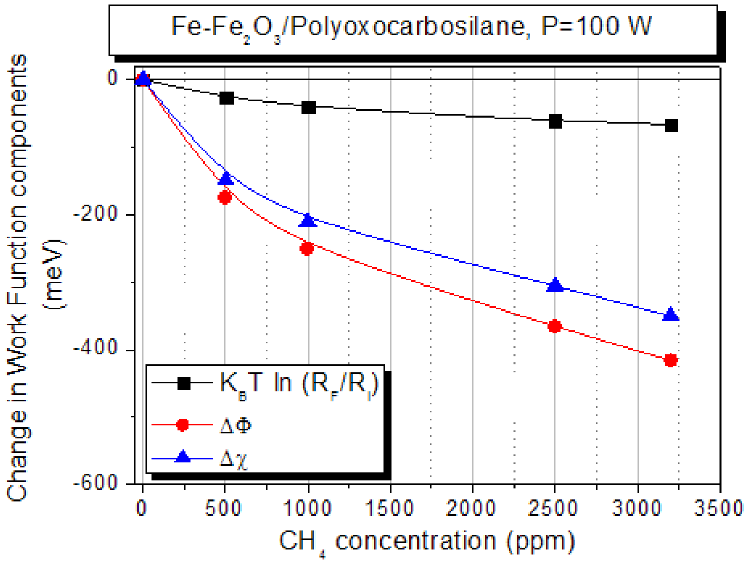

**Fig. 11.** Work Function components for 0–3200 ppm $CH_4$;
RH = 30%, $T_{\text{measure}}$ = 600°C.

## 4. Conclusions

Sensing properties of Polymer-Iron nanocomposite materials are related to both components, which are chemically active in thermal activated conditions. In order to find possible applications, the stability, sensitivity and selectivity are important to be achieved.

For a deep insight understanding of possible interactions during the presence of reducing gases in the atmosphere, complex experimental investigations have been done.

From simultaneous electrical resistance and CPD investigation it was been found a strong influence especially on the electronic affinity upon reducing atmospheres exposure. The surface concentration species which not carrying a net charge (such as dipoles) are the main responsible for the affinity changes of the sensing layer.

However, not only the surface phenomena play an important role in the sensing function. The layer thickness, shape and size of the grains or the metallic electrode geometry also have an important influence in the sensing process.

For porous thick layer, the situation may be complicated further by the presence of three types of contributions: surface/bulk, grain boundary and semiconductor-metallic electrode contact.

The experimental investigations also pointed out the slightly decrease in the band bending for both gases and large scale concentrations.

This raises the questions: on which way the detection takes place (sensing function); the considered sensing model is appropriately or not?

The overall conduction is determined by the role of surface beside the bulk reaction, the resulting charge transfer processes, and not at least the transport mechanism inside the sensing layer.

Therefore, it is important to deepen out insight the in-situ phenomena to provide sufficient information about how the reactions take place, about the mechanisms of the involved phenomena which are not yet fully understood.

Apart of the remained questions, the sensitivity to reducing gases of Polymer-Iron nanocomposite materials were pointed out, together with short response time, short recovery time and good stability in reference air (synthetic air 5.0).

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