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Nanoparticle Langmuir-Blodgett arrays for sensing of CO and NO₂ gases

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Abstract

Metal oxide sensors with active Fe_2O_3 and $CoFe_2O_4$ nanoparticle arrays were studied. Sensing nanoparticle films from 1, 2, 4 or 7 monolayers were deposited by Langmuir-Blodgett technique. Sensors are formed on the alumina substrates equipped with heating meander. Langmuir-Blodgett layers were heated or UV irradiated to remove the insulating surfactant. Sensing properties were studied towards CO or NO_2 gases in concentrations between 0.5 and 100 ppm in mixture with the dry air. Best response values I_{gas}/I_{air} were obtained with $CoFe_2O_4$ device being 3 for 100 ppm of CO and with Fe_2O_3 device being $(38)^{-1}$ for 0.5 ppm of NO_2.

1. Introduction

More than 50 years ago Brattain and Bardeen discovered that semiconductor properties are modified by ambient gas [1]. Seiyama et al. proposed that metal oxide semiconductors could be used in the gas sensors [2]. Since that time the field matured and many devices were developed. Among the monitored gases attention is paid to SO_2, CO, CO_2, CH_4, NO, NO_2, O_2, O_3, Cl_2, C_2H_5OH, H_2O_2 and other air pollutants [3, 4]. Moreover, NO_2 is of primary importance for trace amount detection of explosives like EGDN, TNT, PETN, RDX, etc. [5, 6]. The commercially available explosive sensing machines for ionization and separation analysis of vapours are expensive and employment of dogs is also expensive and complicated. Therefore much effort is paid to electronic sensors. These devices must be extremely sensitive because some explosives have very low vapour pressure. At RT and atmospheric pressure of air it decreases from 50 ppm for EGDN to 30 ppb for RDX and PETN, the pressure of TNT

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and nitroglycerin being 1 ppm and 1 ppb, respectively [5]. From the multitude of oxides for sensing of gases we should mention at least SnO_2 [7, 8], WO_3 [7, 9], $CoFe_2O_4$ [10], Fe_2O_3, Fe_3O_4, In_2O_3 [11] and TiO_2 [12].

Innovative sensors are built from nanoparticles (NPs), nanorods or nanotubes [3, 13]. This way it is possible to increase the surface/volume ratio of the sensing layer. Then the surface scattering is better influenced by adsorbed species and change of sensor conductivity is higher. Baraton and Merhari [3] used SnO_2 NPs to monitor the air quality. The detection threshold of O_3 was as low as 15 ppb and that of CO was 3 ppm. In this work we experiment with sensors from Fe_2O_3 and $CoFe_2O_4$ NPs. In previous papers nanocrystalline $CoFe_2O_4$ for sensors was prepared by hydrothermal method [10] or by electrochemical deposition followed by anodization [14]. Here we have used NPs in the colloidal solution fabricated by chemical route.

2. Experimental

Monodisperse Fe_2O_3 (maghemit) and $CoFe_2O_4$ NPs were synthesized by high-temperature solution phase reaction of metal acetylacetonates (Fe(acac)3, Co(acac)2) with 1,2-hexadecanediol, oleic acid and oleyl amine in phenyl ether at 200 ^oC/30 min plus 265 ^oC/30 min heating [15]. Solvent was toluene. Structure of NPs was studied by grazing incidence (GI) XRD - D8 DISCOVER SSS Bruker and TEM, - JEM 100 C. For these measurements NPs solution was dropped onto Si substrate and dried. Thus, NPs were irregularly arranged and the thickness of the deposit was 10 - 20 NP monolayers (MLs). Size of NPs was estimated using HR SEM Leo 1550. Magnetic properties were studied between 4.2 and 278 K using vibrating sample magnetometer and diluted NP solution in a capillary

NPs Langmuir-Blodgett (LB) films were prepared from the water subphase in the 612 D NIMA trough with two barriers at the surface pressure of 20 mN/m. 1, 2, 4 or 7 ordered LB MLs were deposited by modified (patent pending) procedure. Gas sensors were fabricated on 2 mm × 2 mm alumina substrates. They were equipped with 20 nm Ti/500 nm Pt heating meander on the back side and with 20 nm Ti/200 nm Pt interdigitated electrodes on the front side to read the measuring current. After deposition of the sensing layers the devices were soldered onto a commercial TO-8 socket and they were fixed in a test chamber.

Before measurements samples were held 12 hrs in dry air flux at 400 ^oC to remove the surfactant coverage. Then NP arrays agglomerate which manifests itself by narrowing of diffraction maxima [16]. 1 ML deposit transforms into labyrinth-like structure with certain level of percolation causing the electrical conductivity, 2 ML deposit is almost continuous and 4 and 7 ML deposits aggregate into a compact structure. Alternatively, some samples were treated by UV radiation (4.9 eV). Samples were irradiated 5 min at the flux 2 mW/cm^2 in the ambient of ozone in the dry air. Here the transformed structures better preserve the NP nature [17].

Measurements were performed at different operating temperatures using the heating element. The sensor response to reducing (CO) or oxidizing (NO_2) gas was monitored by an electrometer at a constant voltage of 5 - 10 V between electrodes. The desired concentrations of the gases in air were obtained using certified gas cylinders, mass flow controller and mass flow meters. A total flow of 100 sccm was fixed during the tests.

3. Results and discussion

In the GI XRD spectrum of the Fe-O system the diffraction peaks correspond to either Fe_3O_4 (magnetit, cubic, fcc) or Fe_2O_3 (maghemit, cubic, primitive cell). They have almost similar positions. From the peaks at larger 2 θ angles Fe_2O_3 composition is preferred, cf. [15]. Moreover, under the ageing/heating in the air ambient or UV irradiation Fe_3O_4 is oxidized to Fe_2O_3 [18]. In combination with Co (but also Ni or Cu), ternary compounds $CoFe_2O_4$ ($NiFe_2O_4$ or $CuFe_2O_4$) are formed. They are isomorph with Fe_3O_4 [15]. The diameter of Fe_2O_3/Fe_3O_4 and $CoFe_2O_4$ NPs is 6.4 ± 0.6 and 7.6 ± 0.6, respectively, surfactant is 1.8 nm thick in both cases and blocking temperatures are 22 K and 204 K, respectively. NPs are monodomain and superparamagnetic at RT. Results are similar to those published in [15, 19]. A typical hexagonal-like NP array is shown in Fig. 1.

In Table 1 sensors structure, their working characteristics and properties for two monitored gases are summarized. The interval of working temperatures is 175 ^oC – 475 ^oC. These are temperatures typical for many metal oxide semiconductor sensors [7, 8]. The maxima of the sensor response vs. working temperature for $CoFe_2O_4$

with 7 MLs in Fig. 2 and of other devices in Table 1, respectively, are the consequence of reaching the best dynamic equilibrium between adsorption and desorption of the monitored gas [8, 20]. The base current in air is of
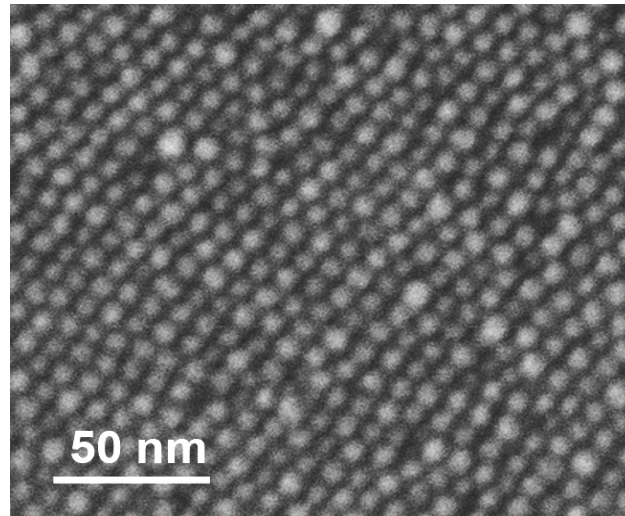

Fig. 1 SEM picture of hexagonal-like $CoFe_2O_4$ nanoparticle array.

Table 1. Structure and operating conditions of sensors with 1, 2, 4 or 7 MLs of NPs (first column). C_g is the gas concentration, T_w is the interval of working temperatures and T_m - maximum response working temperature measured at the concentration C_m. Sensor base current in dry air I_{air} was obtained at T_m or in the middle of T_w interval. The sensor response is $R = I_{gas}/I_{air}$.

NPs/No. of MLs	Gas	C_g [ppm]	T_w [^{o}C]	Tm/Cm [^{o}C]/[ppm]	Iair [A]	R
Fe_2O_3/1	CO	20 – 100	325 – 475	450/100	$3x10^{-9}$	1.3 (400 ^{o}C, 100 ppm)
Fe_2O_3/1	NO_2	5	375	not evaluated	$2.4x10^{-9}$	$(1.8)^{-1}$
Fe_2O_3/2	NO_2	5	450	not evaluated	$1.6x10^{-8}$	$(2.5)^{-1}$
Fe_2O_3/2	NO_2	2	450	not evaluated	$1.6x10^{-8}$	$(1.5)^{-1}$
Fe_2O_3/4 UV	NO_2	4	400	400/4	$2x10^{-8}$	$(280)^{-1}$
Fe_2O_3/4 UV	NO_2	0.5	350	400/4	$9x10^{-9}$	$(38)^{-1}$
Fe_2O_3/7	CO	100	200 – 475	350/100	$6x10^{-7}$	2.8 (350 ^{o}C)
Fe_2O_3/7	NO_2	5	300 – 475	300/5	$8x10^{-7}$	$(8)^{-1}$ (350 ^{o}C)
$CoFe_2O_4$/7 UV	CO	100	250 – 475	425/100	$7x10^{-8}$	3 (350 ^{o}C)
$CoFe_2O_4$/7 UV	NO_2	5	300 -- 475	375/5	$8x10^{-8}$	$(10)^{-1}$ (350 ^{o}C)

the order of 10^{-9} A for 1 ML deposits, which corresponds to not fully continuous labyrinth-like structure. Therefore, we created 2, 4 and 7 MLs deposits. The increase of the base current by 2 orders of magnitude is not a simple consequence of thicker conducting film but predominantly of the formation of continuous structure. The response at the chemisorption of oxidizing NO_2 gas is shown as $(X)^{-1}$, because in this case capturing of electrons from sensing layers in the n – type semiconductor diminishes the conductivity. With reducing CO we have opposite effect [7, 8].

From the comparison of the heat-treated and UV irradiated $CoFe_2O_4$ sensors with 7 MLs of NPs we have seen, that in the second case we have much higher responses for both monitored gases. This is attributed to the preservation of NP structure which is important for increasing the adsorption/absorption capacity of the sensor.

The calibration curves of sensors, i.e. response vs. gas concentration, are linear for all sensing films at T_w approaching to 400 ^{o}C. An example is shown in Fig. 3. At temperatures around 300 ^{o}C 1 ML sensors sometimes show saturation at CO concentration of 100 ppm.
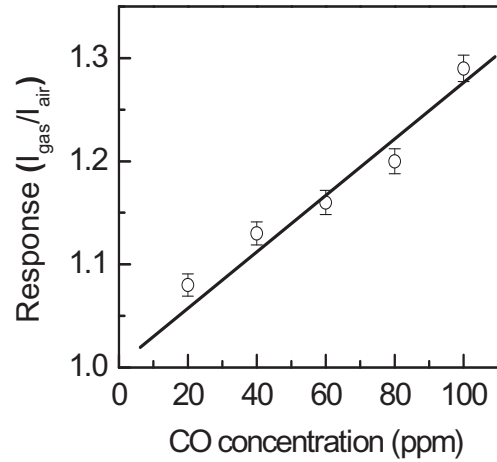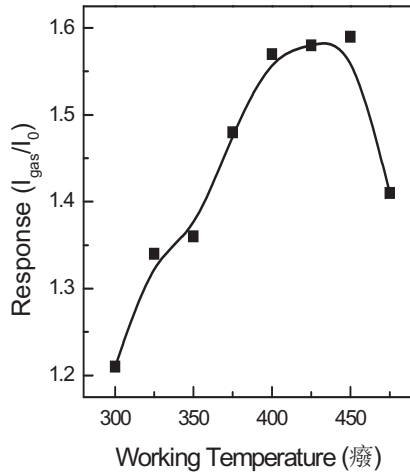

Fig. 2 Response of CoFe$_2$O$_4$ sensor with 7 MLs of NPs vs. working temperature at 100 ppm of CO gas.

Fig. 3 Calibration curve of CO sensor with 1 ML of Fe$_2$O$_3$ sensing film at a working temperature 400 ^{o}C.
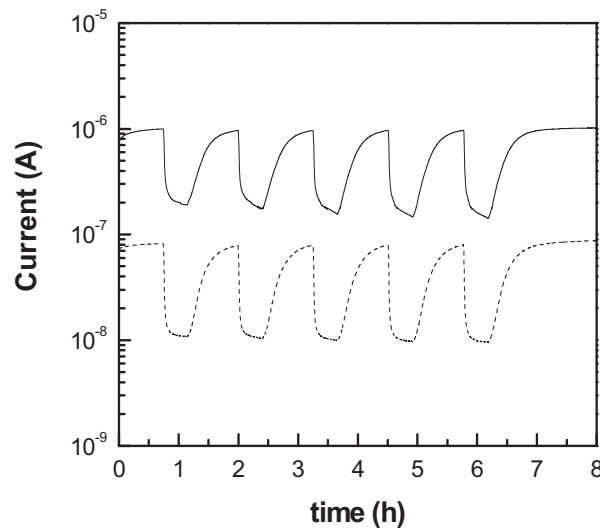

Fig. 4 Dynamic responses to 5 ppm of NO$_2$ at 350 ^{o}C with Fe$_2$O$_3$, 7 ML heat treated sensor (full line) and CoFe$_2$O$_4$, 7 ML UV irradiated sensor (broken line).

In Fig. 4 we have the time dependences of current in heat treated Fe$_2$O$_3$ and UV irradiated CoFe$_2$O$_4$ sensors in oxidizing NO$_2$ ambient. In both cases the signal is quite stable and a good reproducibility is guaranteed. The published response and recovery times of metal oxide sensors are between tens of seconds and tens of minutes as a rule, depending on many parameters, especially on the structure and thickness of sensing film. Short response and recovery times are observed for thin nanocrystalline films where electron processes takes place at the surface [4, 7, 8,

11]. Our results are similar, the times are between 3 and 30 min, being lower for 1 ML sensing films. Also the recovery of sensors is satisfactory (Fig. 4). This is in accord with results of [11], where almost 100 % recovery is reported for Fe – O system. In general, the response of some sensors is very good so that the devices might be of some practical use (Table 1). The results are better than those of monitoring of NO_2 with sensor composed from TiO_2 nanorods [21].

4. Conclusion

We have shown that Fe_2O_3 and $CoFe_2O_4$ nanoparticle based sensors with sensing films composed from 1, 2, 4 and 7 monolayers deposited by Langmuir-Blodgett technique are satisfactory for monitoring reducing CO or oxidizing NO_2 gases at low concentration. With 1 ML films the base current is low because after removing the surfactant the sensing film becomes partly discontinuous. On the other hand films composed from 2 Langmuir-Blodgett monolayers are almost continuous and those from 4 and 7 monolayers form a compact structure. The corresponding sensor current increases with increasing number of monolayers by two orders of magnitude.. The Fe_2O_3 and $CoFe_2O_4$ sensors with response of $(280)^{-1}$ at 4 ppm of NO_2 and $(10)^{-1}$ at 5 ppm of NO_2 , respectively, might be of some practical applications in detection of explosives. Good output of $(38)^{-1}$ was obtained even at 0.5 ppm of NO_2.

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