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SnO_2 and SnAcAc Thin Film Sensors Created by Laser

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Inorganic and organic tin based thin films were created by pulsed laser deposition (PLD) on special alumina chips. Influence of dopants and catalysts was studied. Sensitivity of Sn- based layers to hydrogen, methanol, ethanol, n- propanol and n- buthanol based layers to was measured.

Keywords:

laser deposition; thin film; gas sensors

1. INTRODUCTION

Development of small toxic gas alarms and sensors for ecology, environmental monitoring, chemistry, etc., is one of the interesting goals on which research in various laboratories is concentrated. The structure usually contains active layers based on organic and inorganic compounds (acetylacetonates and oxides of tin and indium, and materials of similar properties), suitable dopants (materials containing ions- Ni^{2+}, Fe^{3+}, Cu^{2+} etc.), catalysts (Pt, Pd, Ni, Fe, etc.) and membranes (polytetrafluorethylene and others). The principle of sensors is based on the variations of DC-resistance with changing concentrations of various gases. Such sensors are usually cheaper in comparison with those based on other

detecting mechanisms. They have also small size, simple operation, and low power consumption and can be easily integrated into other devices.
In this work the sensitivity and selectivity of SnO_2 and SnAcAc based systems is modified by addition of dopants and catalysts. The Sn-based systems are commonly used for detection of reducing gases. The following responses were studied:

a) Sn- based systems to 1000 ppm of hydrogen.
b) Sn- based systems to 1000 ppm of CH_3OH, C_2H_5OH, n-C_3H_7OH and n-C_4H_9OH vapours and 1000 ppm of H_2 for comparison.

2. EXPERIMENTAL

For sensors fabrication small alumina plates having dimensions of 2.5 x 1.5 mm^2 were used in our experiments. On an one side of the plate an interdigital Pt electrodes were created. They serve for reading of sensor response. On the opposite plate side Pt heating element for adjusting of sensor operation temperature was created. For deposition a KrF excimer laser (248 nm wavelength) was used. The sensitivity of active layer was evaluated for temperature of measurement T_m and concentration of detected gas component c_i as a ratio of layer resistance in the air R_{air} and the resistance in the atmosphere containing detected gas at this temperature R_{gas}:

$$S_i(T_m,c_i)=R_{air}(T_m)\,/R_{gas}(T_m,c_i)$$

The PLD deposition process for Sn- based systems was optimised in recent works [1][2]. The highest sensitivity to reducing atmosphere was obtained for an energy density of about 0.6 Jcm^{-2}, laser spot 2.5 x 1.5 mm^2, repetition rate 5 Hz, 5 Pa oxygen deposition background (for SnO_2) and 5 Pa nitrogen background (for SnAcAc).

3. RESULTS AND CONCLUSIONS

a) Response of SnO_2-NiO, SnO_2-NiO-Pd, SnO_2-Fe_2O_3, SnO_2-Fe_2O_3-Pd SnAcAc-FeAcAc, SnAcAc-FeAcAc-Pd_systems to 1000 ppm of hydrogen was studied. The sensitivities reached for various dopant concentrations and addition of catalyst are summarised in Table 1.
Comments to systems a)

- *SnAcAc-FeAcAc and SnAcAc-FeAcAc-Pd :* The adding of FeAcAc leads to an increase of layer resistance together with improving of

measurement reproducibility. On the contrary it causes a slight increase of T_{max}.

- *SnO_2-NiO and SnO_2-NiO-Pd :* With SnO_2-NiO-Pd system the highest sensitivity was reached (S_{max}~ 2820 for 0.1 wt.% of NiO). The sensitivity temperature T_{max} is decreased not only by catalyst, but also by dopant.
- *SnO_2- Fe_2O_3 and SnO_2- Fe_2O_3- Pd systems:* The addition of Fe_2O_3 to basic material causes the increase of sensitivity together with higher selectivity. Introduction of catalysts reduces T_{max} (up to 380 °C for 1 wt. %).

System (basic material-dopant-catalyst)		a - S_{max}, b - (T_{max})			
		0.0 wt.%	0.1 wt.%	1.0 wt.%	10.0 wt.%
SnAcAc-FeAcAc	a	27.5	5.6	5.0	high
	b	(430°C)	(533°C)	(533°C)	resistance
SnAcAc-FeAcAc-Pd	a	174	111	high	high
	b	(383°C)	(413°C)	resistance	resistance
SnO_2-NiO	a	8.8	6.9	8.2	7.2
	b	(485°C)	(444°C)	(430°C)	(443°C)
SnO_2-NiO-Pd	a	1093	2820	253	520
	b	(284°C)	(111°C)	(111°C)	(210°C)
SnO_2-Fe_2O_3	a	8.8	11.2	13.7	1.8
	b	(485°C)	(476°C)	(485°C)	(340°C)
SnO_2-Fe_2O_3-Pd	a	1093	596	127	1130
	b	(284°C)	(193°C)	(100°C)	(105°C)

Table 1: The maximum sensitivity (S_{max}) to 1000 ppm of hydrogen at the temperature of maximal sensitivity (T_{max}) as a function of different dopant concentration (in wt. %).

b) Response of SnO_2, SnAcAc, SnO_2-Pd, SnAcAc-Pd systems to 1000 ppm of H_2 and CH_3OH, C_2H_5OH, n-C_3H_7OH and n-C_4H_9OH vapours is summarised in Table 2.

Comments to system b)

- The SnAcAc- based systems are much more influenced by the presence of Pd catalyst than the SnO_2- based ones. The S_{max} of SnAcAc systems increased in the average two times after sputtering the Pd catalyst.
- The increase of sensitivity is accompanied by decreasing of T_{max} at about 50-100°C.

- The above mentioned effects were not observed for SnO_2-based systems.
- Considering sample with 4 nm of Pd catalyst, it is noticeable that the decrease of detected gas reactivity (from hydrogen to ethanol) leads to decrease of S_{max} and increase of T_{max}. This sample exhibited T_{max} higher than 600 °C when detecting n-propanol and n-butanol, but the reproducibility of the measurements was rather poor at such high temperatures, so their results were not included. Other samples do not show this effect.

Material		H_2	CH_3OH	C_2H_5OH	n-C_3H_7OH	n-C_4H_9OH
SnAcAc	a	11.0	13.7	22.0	6.0	3.6
	b	(456°C)	(526°C)	(538°C)	(538°C)	(559°C)
SnO_2	a	5.2	3.8	3.9	3.1	2.8
	b	(577°C)	(572°C)	(424°C)	(550°C)	(596°C)
SnAcAc+	a	35.3	19.4	50.5	71.2	44.5
2 nm Pd	b	(424°C)	(514°C)	(483°C)	(478°C)	(457°C)
SnAcAc+	a	67.6	20.6	19.8	13.5	17.6
4 nm Pd	b	(424°C)	(477°C)	(466°C)	(478°C)	(478°C)
SnO_2	a	5.3	3.4	2.9	3.3	1.7
+2 nm Pd	b	(351°C)	(478°C)	(558°C)	(393°C)	(383°C)
SnO_2+	a	20.0	7.3	3.8	-	-
4 nm Pd	b	(422°C)	(451°C)	(570°C)		

Table 2: Sensitivity S_{max} (a) of sensor systems to 1000 ppm of hydrogen and alcohol vapors at the temperatures of max. sensitivity T_{max} (b).

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