ԵՐԵՎԱՆԻ ՊԵՏԱԿԱՆ ՀԱՄԱԼՍԱՐԱՆ

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DETECTION OF GASOLINE VAPOR BY ZnO THIN FILM SENSOR

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1. Introduction

ZnO is a wide band gap (3.37 eV) semiconductor. Due to its high thermal and chemical stability, it is widely used in solar cells, optoelectronic devices, semiconductor resistive gas sensors, etc [1-5].

Zinc oxide as a gas sensing material is used in semiconductor gas sensor made of resistive thin film with nanosized grains, nanowires, nanofibers, nanotubes and so on. Such sensors exhibit high sensitivity to various gases (H_2, NO, alcohol, gasoline, toluene, dichlorethan vapors, etc) [6-10].

As we know, gasoline is used in various fields. Especially, it is widely used as a fuel. Cars need in the gasoline high response and selectivity sensors. They should fast detect the gasoline leakage. High precision control of the air-fuel ratio in vapor control system of car engine is necessary [11,12]. There are fuel level non-semiconductor sensors produced in Dongguan Manufacturer, etc. They are complicated, it is necessary to develop microelectronic semiconductor sensors.

It is known that the key parameters of resistive thin film gas sensors depend on the thickness of a sensing layer. Especially, the increase in the response of thin film sensor with decreasing of the sensing layer thickness was observed. Besides, there is an opposite dependence (an increase in the response on the thickness) [13-20]. As we shown below, the first dependence is typical for our samples.

Resistive thin film gas sensors with derrerent thicknesses made of the ZnO–1at%La structure with nanosized grains were prepared by us. The thin film sensor with the film thickness of 80 nm has enhanced response and selectivity to gasoline vapor.

2. Experimental

ZnO-based gas sensing films were deposited by magnetron sputtering method from previously prepared ceramic target. Metal oxide starting materials (powders) were weighted in appropriate quantities (ZnO–1at.%La) and mixed for approx. mately 10 hours. Then, this mixture was subjected to preliminary heat treatment in the 800°C-1100°C temperature range. The resulting mixture was pressed (using the 2000 N/cm^2 pressure) in a form of the 50 mm diameter tablet and annealed. Annealing was performed in software-controlled furnace (Nabertherm, HT 04/16) at different temperatures (1000°C-1400°C). Then, the sample was subjected to mechanical treatment in order to eliminate surface defects and obtain the smooth, parallel target with the appropriate thickness (<2 mm) and diameter (40 mm). The ZnO+1at.%La gas sensitive thin films with different thicknesses were deposited on alumina substrate by the rf magnetron sputtering method using obtained ZnO+1at.%La ceramic target. The growing film thickness was controlled by the changeing of the sputtering time when the power of the magnetron generator unit was fixed. The sputtering duration equals to 10, 15, 30, 45 minutes and the power of magnetron generator unit was 60 W. The substrate temperature during sputtering was 200 °C. Palladium (Pd) catalyst particles (the deposition time was 2 seconds) and interdigited titanium (Ti) contacts (the deposition time was 50 minutes) were deposited by ion beam sputtering method on the surface of the sensing layers. The obtained thin film with sputtering duration of 10 minutes was enough thin (the layer was not continuous) and had an extremely high electrical resistance (10^{12}ohm). The films with sputtering duration of 45 minutes was enough thick (400 nm) and exhibited poor sensitivity to gasoline, toluene and dichlorethan vapors. So, here only the sensing results of the thin films with sputtering duration of 15 and 30 minutes are presented.

3. Results and discussion

The thicknesses of the ZnO+1at.%La films with sputtering duration of 15 and 30 minutes were measured by Ambios XP-1 profilometer, which are 80 and 210 nm, respectively (see Fig. 1). The response (the ratio of the resistance of the sample in air to the resistance in gasoline vapor, R_{air}/R_{gas}) of the semiconductor ZnO+1at.%La sensors to gasoline, toluene and dichlorethan vapors were measured in different temperature range of the work body by gas measurement system [21]. The corresponding responses for the two sensing layers with different thicknesses are presented in Fig. 2. The thinner (80 nm) ZnO+1at.%La based structure exhibits better response to gasoline vapor. The reduction of the sensing layer thickness enhances the sensor response more than four times.

The response of the ZnO+1at.%La film to different concentration of gasoline vapor is shown in Fig. 3. The response of the sensor increases rapidly with increasing in the concentration of gasoline vapor. It is also clear that both the response and recovery times improve with increasing in gasoline vapor concentration.

Fig. 4 shows the resistance change of the ZnO+1at.%La sensor in the presence of 1000 ppm gasoline vapor concentration. It is clear that the response and recovery times are 30 and 130 s, respectively.

The variation of response of the ZnO+1at.%La sensors as a function of workbody temperature is shown in Fig. 5. The sensitivity increase with the workbody temperature increasing was also observed. The plots indicate that there is an approximately linear relation between the response of the La-doped ZnO sensors and the work body temperature for both 80 and 210 nm thicknesses of sensing layers.

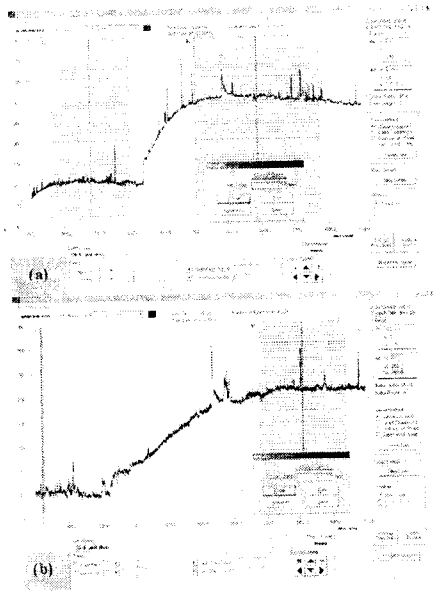

Fig.1.The ZnO+1at.%La films thichnesses measurament resultes with sputtering duration of 15 (a) and 30 minutes (b)

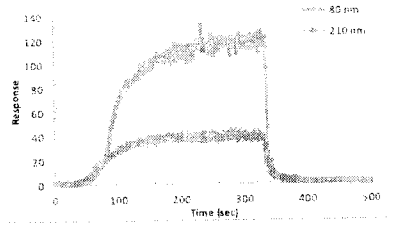

Fig.2.The response curves of the ZnO+1at.%La sensors (with thicknesses of 80 and 210 nm) to 2000 ppm gasoline vapor concentration (the work body temperature was 350 °C).

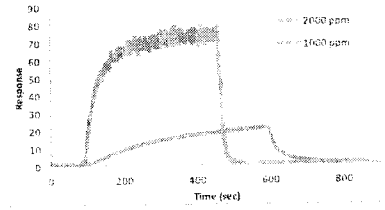

Fig. 3.The real-time response curves of the ZnO+1at.%La sensor (withthickness of 80nm) to various concentration of gasoline vapor (the workbody temperature was 300 °C).

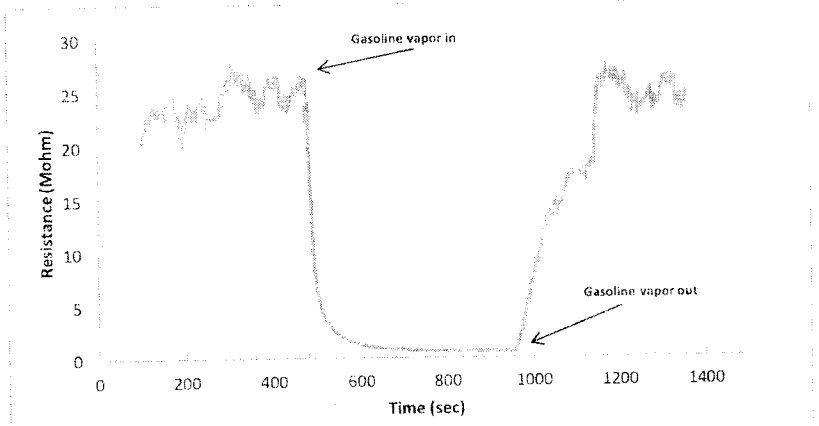

Fig. 4.The variation of the resistance of the ZnO+1at.%La sensor (withthickness of 80nm) for 1000 ppm gasoline vapor concentration (the workbody temperature was 350 °C).

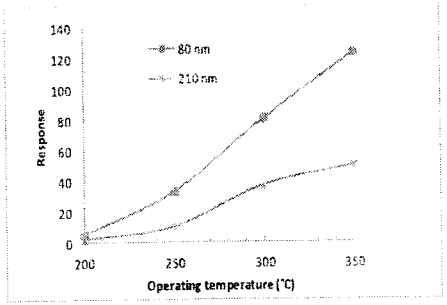

Fig. 5.The relationship of the ZnO+1at.%La sensors response and operating temperature for 2000 ppm gasoline vapor concentration.

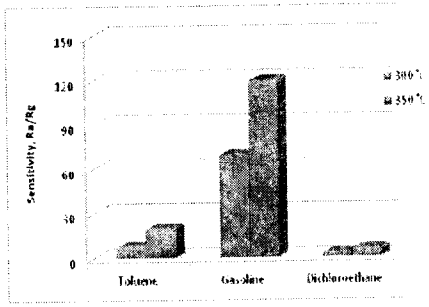

Fig.6. The sensitivity and selectivity of theZnO+1at.%La sensor to different gases (2000 ppm concentration) at different work body temperatures.

It is know that the poor selectivity is serious problem for the practical useable gas sensors. The selectivity of the La-doped ZnO sensor (with thickness of 80 nm) toward other gases such as toluene and dichlorethane vapors was also investigated. The sensor exhibits high selectivity toward gasoline vapor at different work body temperatures (see Fig.6).

4. Conclusion

The La-doped ZnO sensitive thin films with different thichnesses were fabricated by the rf magnetron sputtering technology. The response and selectivity behaviors of the ZnO+1at.%La sensors were investigated. The sensing results indicated that the response of the gas sensor with 80 nm thickness is higher than that of 210 nm. The ZnO based sensor (with 80 nm thickness) exhibits high sensitivity (120) and selectivity to small concentration of gasoline vapor. The response and recovery properties of the sensor are also appreciable. Therefore, it can successfully serves as gasoline vapor detector.

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AUTOMATIC SYSTEM FOR SEMICONDUCTOR GAS SENSOR FLICKER-NOISE MEASUREMENT

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1. Introduction

Flicker-noise (F-N) presents a current or voltage fluctuations, which spectral density changes along with frequency as $1/f^{\nu}$, where value of coefficient ν ranges between from 0.6 and 3 (determined by experiment) [1]. F-N – is a widespread and universal phenomenon in electronic devices. Despite the fact that F-N investigation conducted for a considerable length of time, a general theory of this noise has not been developed yet.

F-N investigations have theoretical as well as a great practical importance, since F-N essentially deteriorates characteristics of electronic constructions and devices, running in low-frequency noise region. F-N can also serve as diagnostic means for semiconductor devices. Successful application of indestractible control method to semiconductor devices by low-frequency noise parameters can be performed with very highquality metrological equipment.

Semiconductorgas sensor (SDS) detection efficiency can be improved bylow-frequency fluctuation-enhanced sensing [2]. Therefore, an example of gas sensor F-N measurement automatic system constructed using LabVIEW graphical program environment is presented in this study.

2. Measurement Method

Noise$u_1(t)$ has extremely small amplitude and therefore requires highamplification.Measurement method idea is in the following – sought-for noise signal $u_1(t)$from investigating gas sensors act on two identical low-noise amplifiers.Considerable own amplifier noise $S(t)$ is incidentally added to amplified noise$U_1(t)$.Therefore chosen measurement method must maximally reduce the effect of amplified noises on measurement result.

One of the noise measurement methods is the following. On Wiring Terminal Board the inputs and outputs of two independent and identical amplifying channels should be connected. This singularly increase the same thing sought for noise signal $U_1(t)$. Since amplifiers' noises are statistically independent, then at correspouding averaging we can exclude amplifiers noise from measurement result. Measurement circuit allows similar averaging based on cross correlation data processing with bi-channel correlative amplifier.

Suppose, there is a sum $U_1 + S_1$on output of first channel with amplification coefficient K, where $U_1(t) = K \cdot u_1(t)$ is the amplified signal; $S_1(t)$ is the own noise of the first amplifying channel. Similarly, on the second channel output – correspondently $U_1 + S_2$. Mutual correlation function $R_{12}(\tau)$is calculated as an average value of amplifier output signal product

$$R_{12}(\tau) = \overline{\big(U_1(t) + S_1(t)\big)\big(U_1(t-\tau) + S_2(t-\tau)\big)}. \tag{1}$$

By multiplying signals under the average symbol we will receive:

$$\begin{aligned} R_{12}(\tau) &= \overline{U_1(t)U_1(t-\tau) + U_1(t)S_2(t-\tau) + U_1(t-\tau)\,S_1(t) + S_1(t)S_2(t-\tau)} = \\ &= \overline{U_1(t)U_1(t-\tau)} + \overline{U_1(t)S_2(t-\tau)} + \overline{U_1(t-\tau)\,S_1(t)} + \overline{S_1(t)S_2(t-\tau)} = \\ &= \overline{U_1(t)U_1(t-\tau)} = R_{11}(\tau), \end{aligned} \tag{2}$$

where $U_1(t)$ is the amplifiers output signals; $S_1(t)$and $S_2(t)$is the noise of the first and second amplifiers. $R_{11}(\tau)$ is the autocorrelation function of $U_1(t)$signal.

In expression (2) all average values of cross products is equal to zero, since factories are statistically independent. Thus this measurement method circuits make it possible to distinguish autocorrelation function of desired noise $\overline{U_1(t)U_1(t-\tau)} = R_{11}(\tau)$ on correlation output.

Energetic spectrum $S_{11}(f) = S(f)$ is determined from one of two equations of Wiener – Khinchin law [1]:

$$S_{11}(t) = 2\int_{-\infty}^{+\infty} R_{11}(\tau)\cdot e^{-i2\pi f\tau}d\tau = F\{R_{11}(\tau)\} \tag{3}$$

Thus, the correlation function R_{11} subjected to Fast Fourier transformation (FFT) according to expression (3), we may receive spectral density $S_{11}(f)$ of the studied noise.

3. Experimental installation and program software

In the virtual instrument (VI) functional diagram of F-N spectrum measurement system according to method discussed above, current noise signal fromthe investigating SGS $u_1(t)$ acts on be-channel low noise amplifier, which is necessary for signal amplification up to input operating range level of analogue-to-digital convertor (Fig. 1).

Correlation amplifiers made and used by us have following parameters: coefficient of amplification is the $K = 10^4$, amplifier bandwidth is the $0 \div 2\ kHz$; input impedance is the 50 MΩ. Amplifiers output signals act on National Instrument Data