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Gasoline sensor based on ZnO

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Abstract

ZnO+1at.%La gas sensitive thin films with different thicknesses were deposited on alumina substrate by the rf magnetron sputtering method using ZnO+1at.%La ceramic target prepared by us. Palladium catalytic particles and interdigited titanium contacts were deposited by ion beam sputtering method on the surface of the sensing layers. The response of semiconductor films to gasoline, toluene and dichlorethan vapors was measured at different operating temperature to 1000 and 2000 ppm gasoline vapor concentration. It was found that the La-doped ZnO sensor with film thickness of 80 nm exhibits high response (120) and selectivity to gasoline vapor (at operating temperature of 350 ^{0}C and 2000 ppm gasoline vapor concentration).

Key words: thin film, magnetron sputtering, gasoline, ZnO, gas sensor

1. Introduction

ZnO is a wide band gap (3.37eV) semiconductor. Due to its high thermal and chemical stability it is widely used in solar cells, optoelectronic devices, semiconductor resistive gas sensors and 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 and 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 by 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. Beside, 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 approximately 10 hours. Then, this mixture was subjected to preliminary heat treatment in the 800^{0}C-1100^{0}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^{0}C-1400^{0}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 derrerent thichnesses were deposited on alumina substrate by the rf magnetron sputtering method using obtained ZnO+1at.%La ceramic target. The growing film thickness was cntroled 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

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magnetron generator unit was 60 W. The substrate temperature during sputtering was 200 ^{0}C. Palladium (Pd) catalytic 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 film 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 wich are 80 and 210 nm respectively (see Fig. 1).

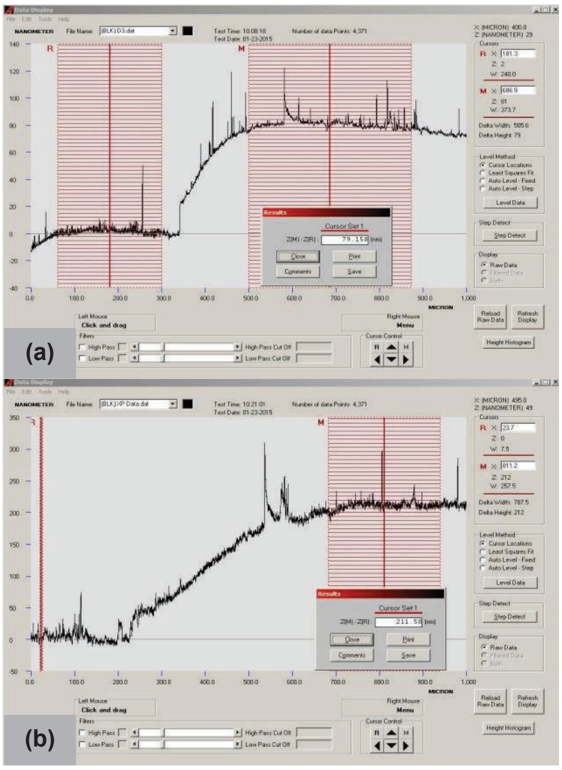

Fig. 1. The ZnO+1at.%La films thicknesses measurament resultes with sputtering duration of 15 (a) and 30 minutes (b).

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 then four time.

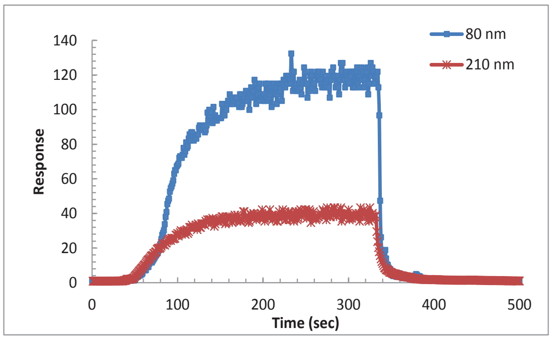

Fig. 2. The response curves of the ZnO+1at.%La sensors (with thicknesses of 80 and 210 nm) to 2000 ppm gasoline vapor concentration (the work body temperature was 350 ^{0}C.)

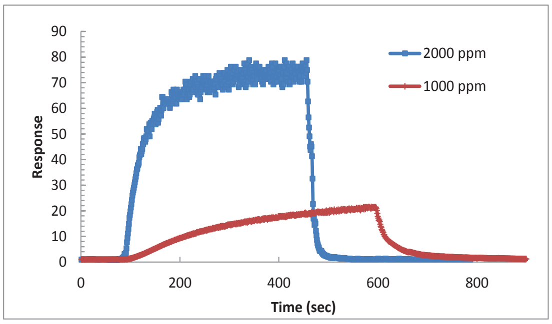

Fig. 3. The real-time response curves of the ZnO+1at.%La sensors (with thickness of 80nm) to various concentration of gasoline vapor (the work body temperature was 300 ^{0}C.)

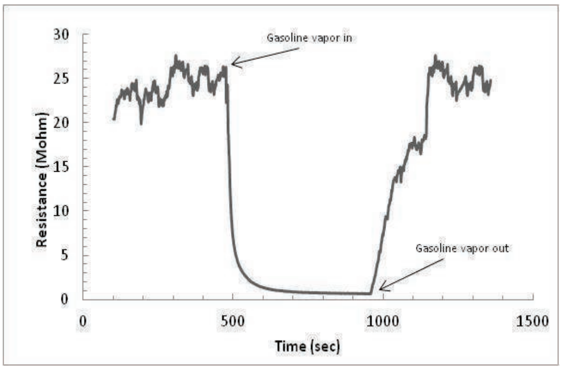

Fig. 4. The variation of the resistance of the ZnO+1at.%La sensor (with thickness of 80nm) for 1000 ppm gasoline vapor concentration (the work body temperature was 350 ^{0}C.)

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 work body temperature is shown in Fig. 5. The sensitivity increase with the work body 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.

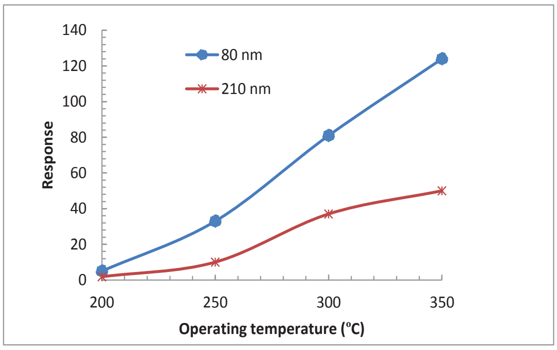

Fig.5. The relationship of the ZnO+1at.%La sensors response and operating temperature for 2000 ppm gasoline vapor concentration.

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).

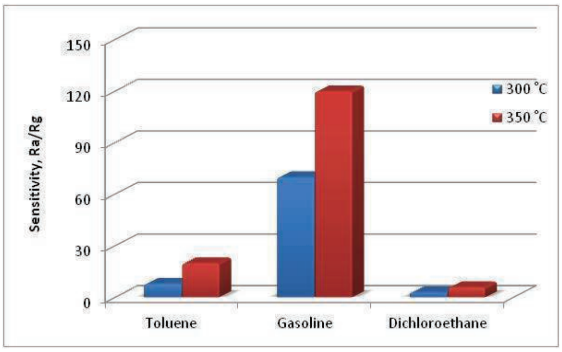

Fig. 6. The sensitivity and selectivity of the ZnO+1at.%La sensor to different gases (2000 ppm concentration) at different work body temperatures.

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 then 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 serve as gasoline vapor detector.

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