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INVESTIGATION OF HYDROGEN SENSOR MADE OF ZnO<Al> THIN FILM

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Abstract — Aluminum-doped ZnO nano-size films were grown on glass ceramic substrates by the high-frequency magnetron sputtering method. Investigations of the surface of films were carried out. Pt layer and gold interdigitated ohmic contacts were evaporated on prepared films by the ion-beam sputtering method. Sensitivity to different concentrations of hydrogen (1000–5000 ppm) in air was investigated. Measurements were carried in the temperature range 40–100°C. The glass ceramic/ZnO<Al>/Pt structure shows sufficient sensitivity to hydrogen at the pre-heating of the working body already up to 40°C.

Key Words: hydrogen sensor, ZnO<Al>

1. INTRODUCTION

Regarding the necessity in detection of different kind of explosive and hazardous gases in the atmosphere, nowadays the gas sensors made of metaloxides and porous silicon using different physical principles are being more used than ever (see, for example, [1-4]). Because of actually used limited energy sources, the demand for sustainable energy sources is becoming more and more especially regards to hydrogen. The demand for the equipments for deciding consists of hydrogen in closed premises and the atmosphere has grown up. Note also that hydrogen is the energy source for the future. It can be used in fuel cell and for other applications. For different equipments, especially for providing safe work of fuel cell, hydrogen sensors which have low energy consumption and low temperatures for pre-heating of working body of sensors are necessary. Nowadays, the technologies for making of hydrogen sensors are being improved. It is important to study new mechanisms which allow making sensors having low prime cost, high sensitivity, selectivity, short response and recovery times as well as small dimensions.

Today the gas sensitivity of thin film structures made of different metal oxide materials (SnO₂, TiO₂, ZnO, etc.) are studied widely [5-10]. It is shown that it is possible to manufacture thin film sensors with the needed small electrical power. Most part of them have the ability to transform the gas concentration change to electrical signal immediately (i.e. electrical resistance or change in conductivity of these materials), which allow using rationally simple scheme for implementing the final equipment. However, the most part of hydrogen-sensitive sensors made of metaloxide materials have high working body pre-heating temperature, which is becoming an obstacle in different setups (especially, in fuel cell) for their use [10-12].

Zinc oxide (ZnO) was used in various form for detection of different gases (see Table 1). As can be seen from Table 1, sensors made of ZnO have high working temperatures.

Table 1. Application of ZnO for detection of different gases.

Work body	gas	t ⁰ C	Ref.
ZnO nanorods	ethanol, hydrogen	350	[13]
ZnO nanowire	ethanol	300	[14]
Al-doped ZnO	NO _x	100-300	[15]
ZnO thin films	methane	150-350	[16]
SnO ₂ -ZnO	ethanol acetone	300	[17]
Fe ₂ O ₃ -ZnO	NH ₃	350	[18]
ZnO	LPG	400	[19]
ZnFe ₂ O ₄	ethanol, acetone	300	[20]

In this work, we tried to realize fast-response hydrogen sensor made of aluminum-doped ZnO having low working temperature and low prime cost.

2. EXPERIMENTAL

As known, ZnO has a relatively high resistivity ($\sim 10^{12}$ Ohm.m). In order to decrease the conductivity of ZnO, we doped it with 1 at% Al. The doping has been done at high temperature according to formula



The mixture of initial powder (ZnO and Al_2O_3) has been mixed for 4 hours. Then it has been compressed under 1000 N/cm^2 pressures. Obtained briquettes of ZnO<Al> were synthesized by the method of solid-phase reactions in air in the programmable furnace Supertherm HT O4/16 with controller C 42. According to chosen by us program, the temperature of the oven has been raised up to 800°C in 2 hours and has been kept during 0.5 hour. After that it has been raised from 800°C to 1200°C in 2 hours and has been kept at this temperature during 3 hours. Hereinafter, the oven's temperature has been decreased up to the room temperature (with the rate of 100°C per hour).

The synthesized ZnO<Al> samples were polished and underwent chemical treatment. These samples were used as targets, which are intended for the manufacture of thin films on glass ceramic substrates by the high-frequency magnetron sputtering method. The power of the magnetron was 80 W, heater current was equal to 20 mA. Hereinafter, platinum layer known for its good catalytic and selectivity properties were evaporated on prepared films by the ion-beam sputtering method. Further the gold interdigitated ohmic contacts were manufactured. The schematic diagram of gas sensor is shown in Fig. 1.

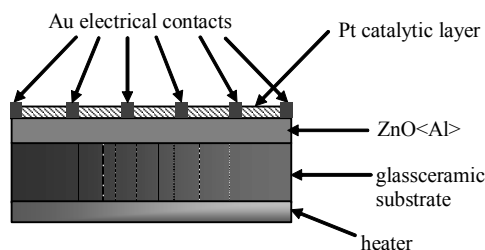


Fig. 1. Schematic diagram of gas sensor.

The thickness of prepared films was measured using Ambios XP-1 Stylus Profiler. Investigations of the surface of films were carried out using SEM Vega 5130 MM (TESCAN) microscope.

Aluminum-doped ZnO films were manufactured on glass ceramic substrates. This allows obtaining ZnO thin films with rather small sizes of grains [21]. The thickness of films was equal to 80 nm. The SEM image of prepared ZnO<Al> films is shown in Fig. 2. The SEM analysis shows that obtained ZnO<Al> thin films had typical grain sizes of $\sim 20\text{--}30$ nm.

The study of samples' sensitivity has been carried out in a close chamber. For the beginning, the air pressure was equal to the atmosphere. For measuring the samples' sensitivity regarding to hydrogen a gas mixture which consist of 5% H_2 and 95% N_2 has been thrown to space. The quantity of H_2 in the chamber was 1000–5000 ppm (or 0.1–0.5 %). During the measurements, the voltage value was equal to 1 V. The sensitivity of the samples has been measured in the range of working body temperature from room up to 100°C . During measurements, gas input and change of samples' temperature have been controlled by the automated measurement system.

3. RESULTS AND DISCUSSION

The samples showed sensitivity to H_2 starting from 40°C . As a unit for sensitivity, it has been decided to have the ratio $R_{\text{air}}/R_{\text{gas}}$, where R_{air} is the conductivity of sample in air, and R_{gas} is the

conductivity of sample in the atmosphere of hydrogen gas. In Fig. 3 samples' sensitivity changes depending on time from 40 to 100°C at different concentrations of hydrogen are shown.

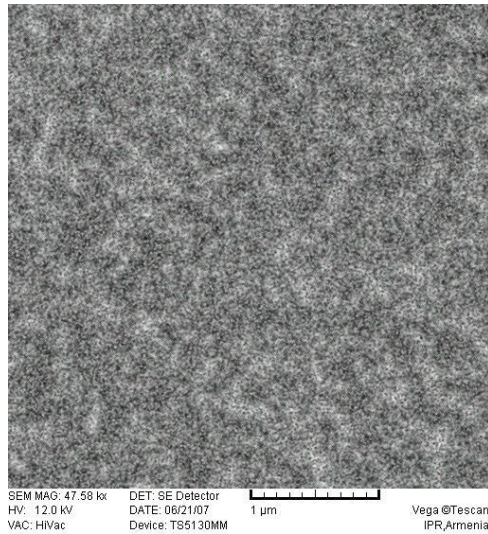


Fig. 2. SEM image of ZnO<Al> thin film.

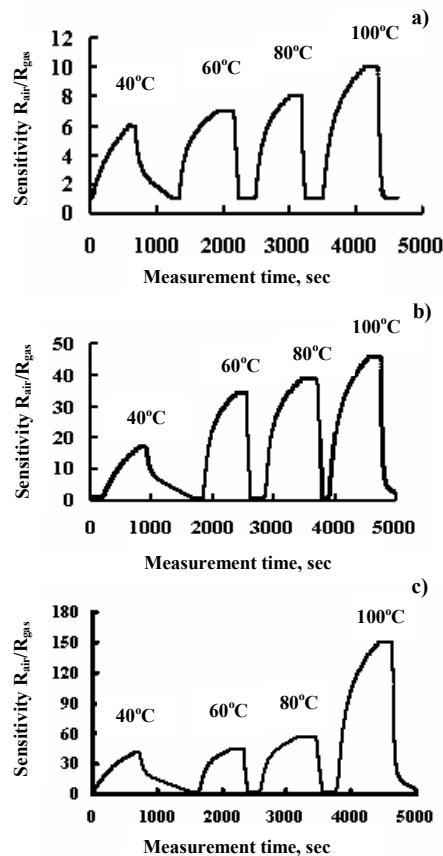


Fig. 3. Sensitivity of the glass ceramic/ZnO<Al>/Pt structure to hydrogen at different temperatures. Concentration of hydrogen was 1000 (a), 3000 (b) and 5000 (c) ppm.

It is seen from Fig. 3 that the samples have high sensitivity in the case of low concentrations of hydrogen in air (1000 ppm or 0.1%), which is one of the main pre-conditions in the field of manufacturing of explosive gas sensors, as only in this case it is possible to avoid an input of gas with such concentration which can bring to explosion. Besides, from these dependences it can be seen that starting from 60°C the samples have short response and recovering times. It was mentioned that fast-

response for explosive and hazardous gas sensors is also an important parameter, in order to be able to avoid the gas input into the atmosphere on the right time. It also can be seen from Fig. 3 that the recovery time is shorter than the time of response.

Nowadays, high sensitivity and fast response of well-known gas sensors is being provided by high temperatures of preheating of the working body. But in most of them, the recovery time at that working temperature is so long (sometimes, it can reach hours), that for the aim to shorten this time the temperature of working body of sensors raised from its real working temperature (double or more) for a while, which is becoming as additional obstacle for their use. From mentioned results, it can be seen that the recovery time in obtained by us structures is shorter than the response time, which is good result.

The high sensitivity and fast-response of hydrogen sensitive sensors made of Zn<Al> films can be explained in the following way. Even 50 years ago Mollwo [22] observed that exposure of ZnO by hydrogen caused a noticeable increase in the conductivity of the material. The calculations in [23,24] showed that hydrogen behaves exclusively only as a donor H^+ in ZnO. It was shown in [25] that such situation may arise also in InN while interacting with hydrogen. In case of other known semiconductors hydrogen acts exclusively like some impurity level lying in the band gap. Only in case of interacting with InSb and GaSb shallow donors of hydrogen electrons are inside the InSb and GaSb valence band. So, in case of other semiconductors, the shallow donors of hydrogen electrons are localized in the band gap. The shallow donor of hydrogen in ZnO is above of the conduction band edge and H^+ is the only stable charge state. Hydrogen always gives up its electrons, as a result of which the concentration of free electrons increases.

For checking the selectivity of manufactured structures made of ZnO<Al> thin films, their sensitivity has been also studied in a close chamber in the presence of propane and butane gas concentrations of 1000–5000 ppm at the temperature region from room temperature up to 200⁰C. The results have shown that in such conditions this structure is not sensitive to propane and butane gases.

The change of samples' conductivity has been also measured (which we accepted as samples' sensitivity) in the case of 50–90% humidity. As a result, there is no noticeable change in samples conductivity.

4. CONCLUSION

Thus, aluminum-doped ZnO thin films were manufactured on glass ceramic substrates by the high-frequency magnetron sputtering method. The obtained ZnO<Al> thin films have nano-size grains (~20–30 nm). The glass ceramic/ZnO<Al>/Pt structure showed sufficient sensitivity to hydrogen at the heating of the working body already up to 40⁰C. The investigations have shown that this structure has fast response and recovery time periods starting from 60⁰C. We have shown that in contrast to many other metaloxide materials, using our aluminum-doped ZnO films, it is possible to realize hydrogen sensors with remarkable low temperatures of pre-heating of the working body. The structure obtained satisfies the basic requirements to gas sensors. Such structures can be used in manufacturing of “electronic nose” as well.

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