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Sensors and Actuators B 124 (2007) 62–67
SENSORS AND ACTUATORS B CHEMICAL
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Fast response methane sensor using nanocrystalline zinc oxide thin films derived by sol–gel method

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Received 3 July 2006; received in revised form 22 November 2006; accepted 24 November 2006
Available online 8 January 2007

Abstract

Undoped nanocrystalline n-ZnO thin films were deposited on SiO_2-coated p-Si substrates by sol–gel technique to fabricate ZnO-based resistive sensors for methane detection. The resistance change was studied at different temperatures (50, 150, 200, 250, 300 and 350 °C) with two different metallic contacts to ZnO, e.g. gold and palladium-silver, in air and in the presence of three different concentrations (0.1, 0.5 and 1%) of methane in N_2 carrier gas. The response, response time and recovery time were studied in detail. A significant improvement of the sensor performance was observed with a Pd-Ag (26%) contact. The maximum response of 74.3% and the lowest response time of 16.3 s were obtained at 250 °C using the Pd-Ag (26%) catalytic metal contact to ZnO. The mechanism of sensing by ZnO was suggested similar to that of the SnO_2 sensors reported by Yamazoe.

Keywords: Sol–gel; Nanocrystalline zinc oxide; Methane sensor; Pd-Ag (26%) contact; Fast response

1. Introduction

Methane gas is highly volatile when mixed with air and can cause explosions due to ready inflammability. Methane may also displace oxygen to cause asphyxiation in cramped or inadequately ventilated areas. In addition, it has recently been reported that methane is about 20 times more effective greenhouse warming gas than carbon dioxide [1]. Thus, the development of a reliable and cost effective methane gas sensor remains a promising problem for timely detection of its conspicuous presence in the environment around us and in the coalmine atmosphere to save human life.

Semiconducting oxides like SnO_2 [2–4], Ga_2O_3 [5], Co_3O_4 [6], etc., were reported for detection of methane, but the sensing temperature reported is quite high (∼350–450 °C) [2–5], which is inconvenient for using the sensors particularly in mining environment where high temperature may cause explosions. It may also incur higher power consumption [7] and short battery lifetime. Moreover, the response time of few tens of seconds to minutes with the above sensors have been reported [2,5,6].

ZnO is a versatile material having applications in the areas like SAW devices [8], varistors [9], transparent electrodes [10], optoelectronics [11], etc. Several reports have already been published on the gas sensing properties of ZnO [12,13]. This is usually an n-type compound semiconductor with hexagonal wurtzite structure and a wide band gap (∼3.2–3.4 eV) at room temperature [14]. ZnO thin films can be conveniently deposited on various substrates by well-known methods like sputtering [15], spray pyrolysis [16], CVD [17] and sol–gel [18]. The stoichiometry and doping can control the conductivity of ZnO. Moreover, ZnO is well lattice matched with Si for standard CMOS technology. Very few reports have so far been published on methane sensors based on ZnO [19,20]. Although Nunes et al. published a report on ZnO sensors for methane detection at low temperatures (100–200 °C), no detailed study on dynamic response behavior was reported [19].

In this paper, we report on the deposition of nanocrystalline ZnO thin films on SiO_2-coated p-Si (for possible integration with standard CMOS technology) by a sol–gel method and its application as a methane sensor. The sensor study in the resistive mode was performed at different temperatures (50, 150, 200, 250, 300 and 350 °C) and at different methane concentrations (0.1, 0.5 and 1%). The response and the response time as a function of methane gas concentration were studied at optimum tempera-

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doi:10.1016/j.snb.2006.11.046

ture. Both Au and Pd-Ag (26%) were used as a metallic contact to the ZnO layer. The Pd-Ag contact was found to produce a relatively lower optimum temperature of 250 °C for the maximum response and short response time. It was further observed that the sensor could also exhibit an appreciable response (∼44%) and an acceptable response time (∼65 s) at a temperature down to 150 °C. On the other hand, an Au contact showed 350 °C as the optimum temperature for the maximum response (∼54%).

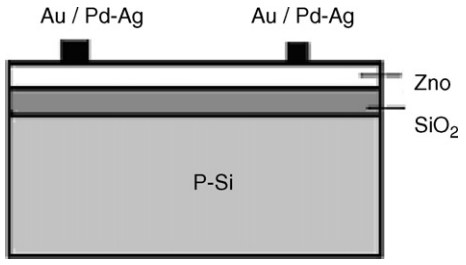

Fig. 1. Schematic of the sensor structure with an Au or Pd-Ag (26%) contact.

2. Experimental

0.45 M Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) (98%) was mixed with isopropanol and was stirred at room temperature. When the solution turned milky, diethanolamine (DEA) was added slowly to yield a clear transparent homogeneous solution [21]. After aging for 24 h, the solution was subjected to spin coating on the SiO_2 thermally grown over p-Si (resistivity 1 Ω cm, 400 μm thick) substrates with a dimension 4 mm × 4 mm. The rotation speed of the coating unit was 1000 rpm and the duration of the single coating was 25 s. Then the samples were heated at 110 °C for 10 min to evaporate the solvent and to remove organic residuals. Finally, the samples were annealed at 600 °C for producing nanocrystalline ZnO. The entire process was repeated for three times and a ZnO film of ∼900 nm thickness with the particle size ranging from 45 to 75 nm was produced. X-ray diffraction (XRD) measurements (Phillips PW 1730/10) of ZnO films were carried out using Cu Kα (λ = 0.15404 nm) as the source line. The scanning electron microscopic (SEM) images were taken using a JSM-5600 (JEOL) scanning electron microscope.

Two different configurations were made for sensor study. In one Au and in the other Pd-Ag (26%) were deposited on ZnO by an e-beam deposition method (10^{-6} mbar) using Al metal masks. The contact area was kept 2 mm × 2 mm in both cases. The schematic of the sensor configuration is shown in Fig. 1.

The sensor characteristics were studied inside a closed glass tube (10 cm × 4 cm ϕ) with inlet and outlet for gases and it was placed coaxially inside a resistively heated furnace with a 4 cm constant temperature zone. The temperature was controlled within ±1 °C using a copper constantan thermocouple in-built in a precise temperature controller. Electrical connections were taken by using fine copper wire and silver paste for the metallization contacts.

For sensor study high purity (100%) methane gas and IOLAR grade N_2 in desired proportions were allowed to flow to the gas-sensing chamber through a mixing path via an Alicat Scientific mass flow controller and a mass flow meter for keeping the mass flow rate and thus the concentration of the methane gas constant throughout the experiments. The schematic of the sensor measurement setup is presented in Fig. 2. The gas pressure over the sensor device was 1 atm during the experiments. The resistance of the sensors in the presence and absence of CH_4 was measured by a Keithley 6487 picoammeter/voltage source.

3. Results and discussion

Fig. 3 shows the X-ray diffraction pattern of the ZnO film deposited by the sol–gel method and Fig. 4 shows the SEM micrograph of the same film. The XRD pattern indicates the growth of the film along the five planes of orientation (0 0 2), (1 0 0), (1 0 1), (1 0 2) and (1 1 0). The most preferential growth occurred obviously along the *c*-axis (0 0 2) plane. The surface morphology studies reveal randomly oriented grains having hexagonal structure with an average size of 45–75 nm with a substantial amount of pores having an average diameter of 56 nm which is very useful for methane gas sensing. It was observed that for the film in the thickness range 300–600 nm, the quality of the film was deteriorated substantially at higher temperature (350 °C), thereby destroying the sensor structure even with short time operation. But the film of 900 nm thickness was quite stable and so all the measurements were done with 900 nm thick ZnO films.

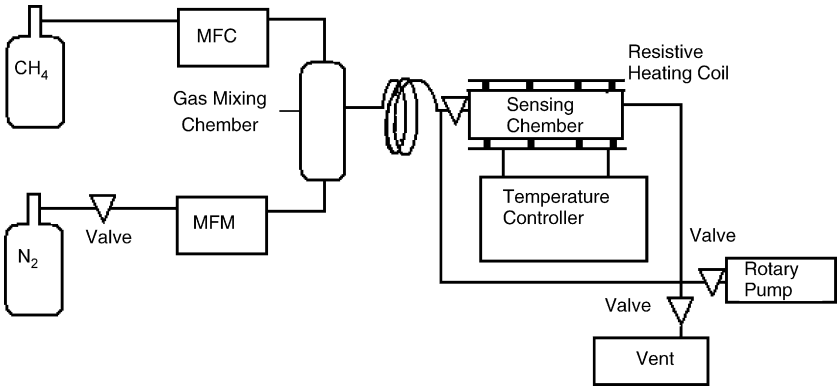

Fig. 2. Schematic of the gas sensor measurement setup.

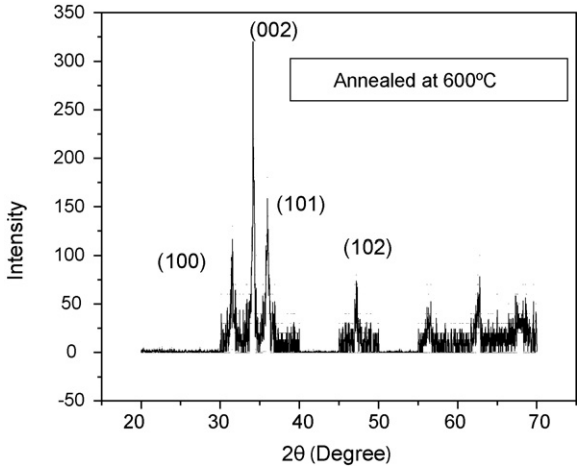

Fig. 3. The XRD pattern of the nanocrystalline ZnO surface annealed at 600 °C for 30 min.

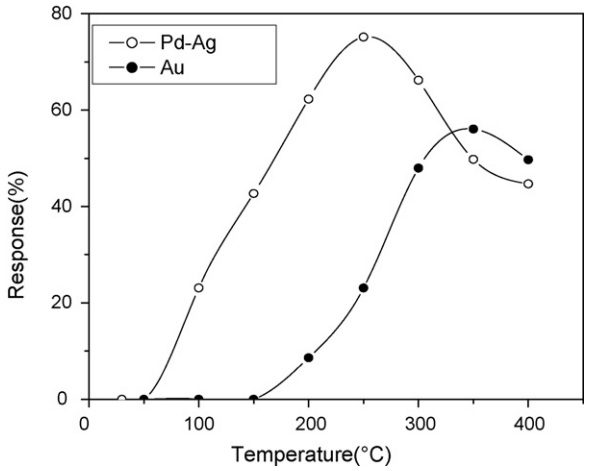

Fig. 5. Response to 1% methane as a function of temperature.

Systematic gas sensing studies were made on ZnO thin films using both Au and Pd-Ag contacts. Initially the response to 1% CH_4 was recorded at different operating temperatures. The response S is expressed in terms of sensor resistance in air (R_a) and in test gas (R_g) as follows [22]:

$$S = \frac{R_a - R_g}{R_a}$$

The response time is defined as the time to reach 67% of the saturation response.

The response as a function of operating temperature to 1% CH_4 for both types [Au and Pd-Ag (26%)] of contacts to ZnO are shown in Fig. 5. It clearly shows that the temperature for the maximum response was brought down from 350 °C with an Au contact to 250 °C by using the Pd-Ag contact. Moreover, the maximum response increased from 56.1% (Au) to 74.3% (Pd-Ag). Another important observation was that though the maximum response (with Pd-Ag contact) is obtained at 250 °C, the sensor shows a quite moderate response (44%) and response time (65 s) even at 150 °C. With an increase in temperature above 250 °C, the response decreased. This behavior can be explained from the kinetics and mechanism of gas adsorption and desorption on the ZnO or similar semiconducting metal oxide surfaces [23].

Fig. 6 shows the variation of response as a function of methane concentration for both types of contacts. It is apparent from the figure that there is an increasing trend of response upon exposure to higher methane concentrations eventually reaching saturation. The same adsorption–desorption kinetics plays the pivotal role with the sticking coefficient initially increasing with increasing CH_4 concentration, followed by a decreasing trend at very high methane concentrations. It was observed that the Pd-Ag contact is more efficient for sensing lower concentrations of methane.

The transient response behavior of the sensor structures in 0.1, 0.5 and 1% methane for an Au contact at 350 °C and for Pd-Ag at 250 °C are shown in Fig. 7(a and b), respectively. Upon exposure to methane the sensor resistance initially decreased due to the release of free electrons and then got saturated, while on cutting off the methane supply the resistance increased and returned nearly to its baseline value. Fig. 7 shows that they do not reach exactly the baseline value possibly because of some gas molecules remaining adsorbed on the sensor surface. The calculated values of response, response time and recovery time

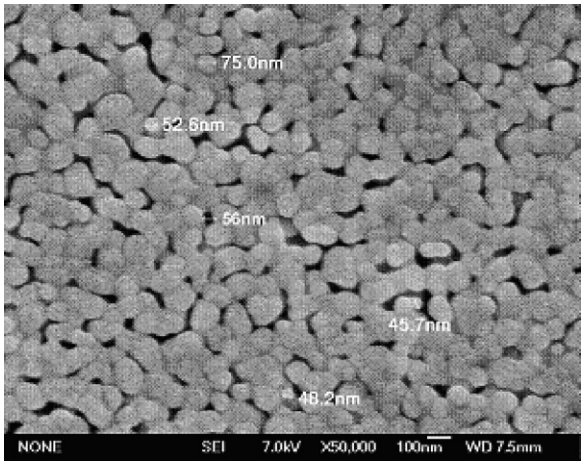

Fig. 4. SEM images of the nanocrystalline ZnO surface annealed at 600 °C for 30 min.

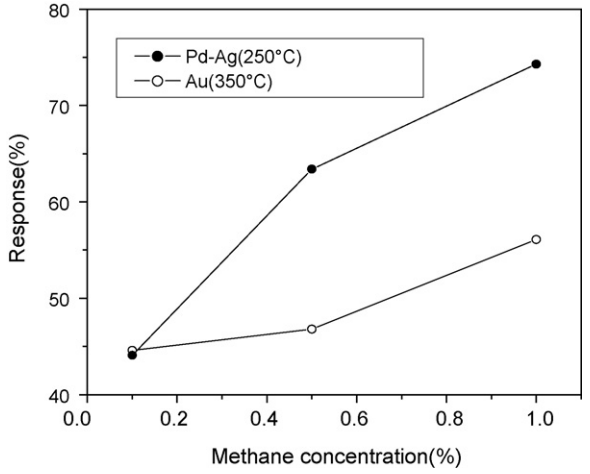

Fig. 6. Response as a function of methane concentration.

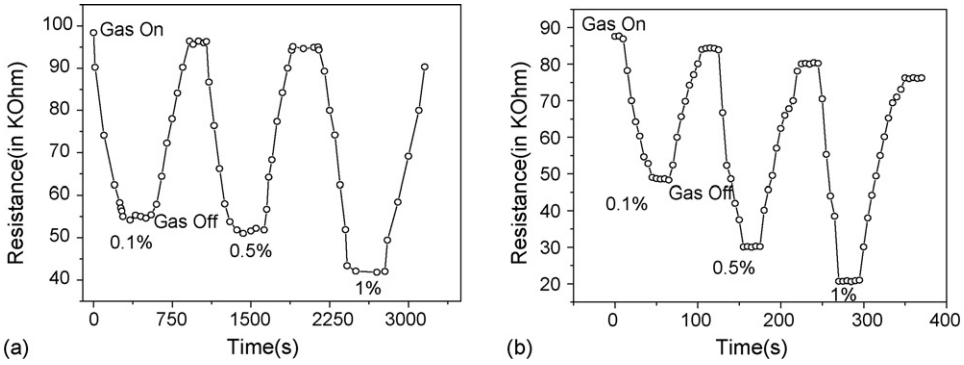

Fig. 7. Transient response characteristics with (a) Au contact (b) Pd-Ag contact.

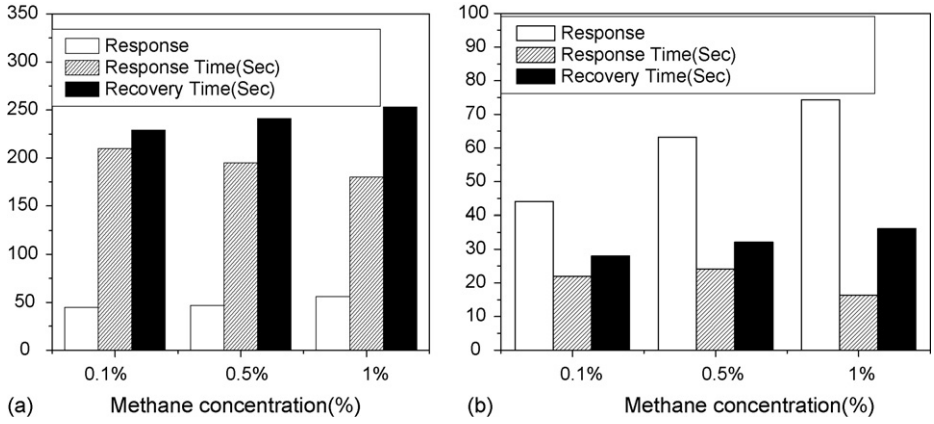

Fig. 8. Response, response time and recovery time as a function of gas concentration for (a) Au contact (350 °C) and (b) Pd-Ag (26%) contact (250 °C).

for different gas concentrations are plotted in Fig. 8, which shows that the values improve significantly with the Pd–Ag alloy contact.

As expected, our results show that the response, response time and recovery time are the functions of methane concentrations. An increase in methane concentration provides more methane molecules to be adsorbed on the oxide surface per unit time, thereby favoring the fast electron transport kinetics, as a result of which the response increases and the response time decreases. On the other hand, the recovery time is longer due to slow desorption kinetics of the methane gas from the interface at higher concentrations.

The results indicate that the response, response time and recovery time for the ZnO-based methane sensor were not so striking with an Au contacts. Moreover, operating temperature was also quite high (350 °C). The response, response time and operating temperature (250 °C) of the sensor structure have been significantly improved by incorporating Pd-Ag as a contact to ZnO, due to the fact that Pd is a good catalytic metal for oxidation of H_2, CH_4 and other hydrocarbons. Ag was alloyed with Pd to prevent the formation of palladium hydride, which affects the Pd/ZnO interface property and thus the stability of the sensor. Nevertheless, Ag was also added to the catalytic effect to Pd, will be discussed later.

Table 1 shows the response, response time and recovery time of the sensor with a Pd-Ag (26%) contact at different methane concentrations and at different operating temperatures. To 1% methane the maximum response of 74.3% was obtained at 250 °C, whereas the minimum response and recovery time were found to be 16.3 s (1% CH_4) and 28 s (0.1% CH_4), respectively.

Table 1
Response, response time and recovery time at different gas concentrations and at different operating temperatures of ZnO with a Pd-Ag (26%) contact

Temperature (°C)	Response time (s)			Recovery time (s)			Response (%)		
	0.1%	0.5%	1%	0.1%	0.5%	1%	0.1%	0.5%	1%
150	106	98	65	122	129	146	24	30	44
200	54	47	27	76	88	92	28	33	46
250	**22**	**20.1**	**16.3**	**28**	**32.1**	**36.1**	**44.1**	**63.3**	**74.3**
300	38	35	28	44	47	56	34	42	51
350	46	43	37	53	58	64	31	39.5	48

The bold values correspond to the optimum operating temperature of our sensor. At this temperature (250 °C) the sensitivity is maximum and response/recovery time is minimum.

So far the reported sensor structures based on different types of semiconducting oxides and mostly working in the resistive mode are operated either at high temperature with appreciably long response time or at low temperature without any information on response time. For example, Fleischer and Meixner [5] reported on a Ga_2O_3-based methane sensor, which was operated at 420 °C with a response time of the order of minutes. Wöllenstein et al. [6] have reported Co_3O_4-based sensors operating at 240 °C with a response time of 6 min. Nunes et al. [19] reported a ZnO-based methane sensor at a relatively lower operating temperature of 100 °C, but without any information on the dynamic response characteristics. Our results showed that the optimum operating temperature of sensing is moderately low (250 °C) and the response time is also appreciably fast (∼16 s).

A possible mechanism for methane sensing in the present study is depicted as follows. It is known that addition of a small amount of noble metal, e.g. Pd or Pt, to the metal oxide can promote not only the gas sensitivity but also the rate of response to a great extent due to the catalytic activities of these metals for oxidation of inflammable gases like methane. According to Yamazoe [24], Pd and Ag act as an electronic sensitizer as they affect the work function of SnO_2 during gas sensing. Following the same arguments, we can envisage that the work function of ZnO shifts (increases) in the presence of Pd and Ag in air, thereby widening the depletion region on the ZnO–Pd (Ag) interface, as indicated in Fig. 9. However, this shift vanishes when the samples are exposed to methane or similar reducing atmosphere. Fig. 10 clearly depicts that there is a change in the ZnO Fermi level in the presence of hydrogen, thereby reducing the band bending facilitating the electron transport. As reported by Kohl [25], methane dissociates to a methyl group and hydrogen, followed by combining the adsorbed hydrogen atoms producing hydrogen molecule, as shown below:

$$CH_{4gas} \leftrightarrow CH_{3ads} + H_{ads}$$

$$H_{ads} + H_{ads} \leftrightarrow H_2$$

The hydrogen molecule then reacts with the adsorbed oxygen on the Pd (Ag) surface (shown in Fig. 9) and produces H_2O. The adsorbed organic radicals undergo a chain of reactions and finally produce CO_2 as another product.

Silver was primarily alloyed with Pd to prevent the formation of palladium hydride in the presence of hydrogen coming from methane [26]. Palladium hydride has poor lattice matching with ZnO and as a result Pd may be chipped off from ZnO, thereby damaging the Pd–ZnO interface. As reported in the literature, since silver has a similar sensitizing property to Pd [24], it may be expected that the Ag added may further sensitize the surface catalytic reaction apart from improving the interface property significantly.

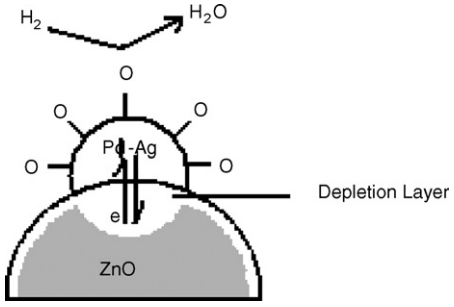

Fig. 9. Sensitization mechanism of Pd-Ag/ZnO sensor.

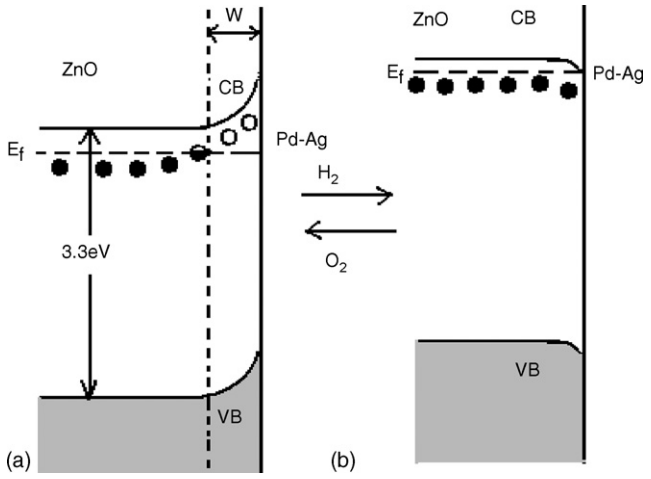

Fig. 10. Schematic band diagrams of Pd-Ag/ZnO in (a) oxidized state and (b) reduced state.

4. Conclusion

Methane and other hydrocarbon sensors, so far reported in the literature, are mainly based on SnO_2. In this report, nanocrystalline zinc oxide thin films produced by well-known sol–gel method were found to produce an efficient resistive gas sensor for methane sensing. A Pd-Ag catalytic contact to zinc oxide showed a quite high response (∼74%) at 250 °C and a response time of ∼16 s, which is much shorter than the reported results showing in the order of minutes.

Acknowledgements

One of the authors (P. Bhattacharyya) gratefully acknowledges the CSIR, India, for a Senior Research Fellowship (SRF). The work has been carried out under the research project sponsored by DST, Govt. of India.

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