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ZnO Based Gas Sensors for Alcohol Sensing

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Abstract
Sensor technology is one of the most significant technologies for the future with a constantly growing number of applications, ranging from toxic gas detection, manufacturing process monitoring to medical diagnosis and health monitoring. Among the different existing sensor technologies, the semiconductor sensors are most attractive for their high sensitivity, small size and light-weight construction. Also they are cheap, rugged and simple in operation which makes them suitable for a large number of applications. The n-type metal oxides like SnO_2, ZnO, Fe_2O_3, Ga_2O_3, In_2O_3, WO_3 are generally used as sensing material for semiconductor sensors. Pure zinc oxide was almost insensitive to ethanol. In this paper, the alcohol-sensing mechanism of ZnO has been studied.
Keywords: Zinc Oxide based Alcohol sensors, Gas Sensor, Alcohol, Catalytic Oxidation.

Introduction

Zinc oxide (ZnO) is a wide band gap (3.37 eV) semiconductor with a large exciton binding energy (60 eV) [1], and an exceptionally important material for applications in Silicon based solar cells, solid-state optoelectronic devices, and so on [2,3]. ZnO materials have been widely used as dielectric ceramic, pigment, catalyst and sensing material [4]. Presently researchers also focused on gas sensing properties of ZnO. ZnO gas sensing properties has now become highlighted because of its high mobility of conduction electrons, good chemical and thermal stability, low-cost [5,6]. Semiconductor gas sensors are widely used for the detection. In recent years, the studies on ZnO gas sensing materials, which can improve its preparation method and decrease its working temperature, are one of its major research topics [7].

The sensitivity of metal-oxide gas sensors can be considerably improved by dispersing a low concentration of additives, like Pd, Pt, Au, Ag, Cu, Co, and F [8] on oxide surface or in its volume. Though doping has been used for a long time now in preparation of viable gas sensors, the working principle of additive-modified metal-oxide materials is still not completely understood. Basically there are two general schemes of the gas sensing mechanism one is chemical scheme the reaction occurs at the oxide surface other one electronic mechanism the reaction provides the dopant atoms, and the oxide material has to transduce the electrochemical changes into a detectable output signal.

Different methods for sensing alcohol using zinc oxide based sensors are studied. Firstly, Hongsith et al.[9] proposed ZnO nanobelts on copper tube by radio frequency (RF) sputtering. The ethanol sensing properties of ZnO nanobelts were observed from the resistance change under ethanol vapor atmosphere at different ethanol concentrations and at temperature of 200–290°C. After that Chou et al.,presented[10] the ZnO:Al thin films by RF magnetron sputtering on Si substrate using Pt as interdigitated electrodes. Patil et al.[11] studied thick films of pure zinc oxide by the screen printing technique. Pure zinc oxide was almost insensitive to ethanol. Thick films of Al_2O_3 (1 wt%) doped ZnO were observed to be highly sensitive to ethanol vapours at 300°C. Wang et al.[12] proposed the nanostructures and gas-sensing properties of Zinc oxide nanosheets prepared by hydrothermal method. A survey on zinc oxide based alcohol sensors is carried out and their different parameters like sensitivity, stability, response time, etc. are studied and compared. In this paper, the alcohol-sensing mechanism of ZnO was studied.

The typical metal-oxide gas sensor element consists of the following parts: 1. Sensitive layer, 2. Substrate, 3. Electrodes, and 4. Heater

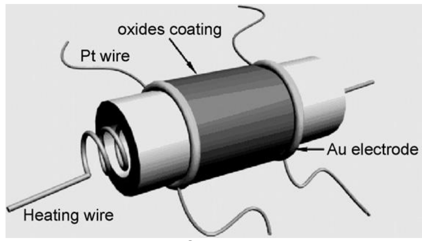

Fig.1 Sketch of the gas sensor structure.

Principle of Operation

The sensors frequently change their resistance by more than a factor of 100 upon exposure to a trace of reducing gases like hydrogen, methane, ethanol, carbon monoxide and propane. Incidentally, the free electrons of n-type semiconductors like ZnO are trapped by oxygen from the ambient by its e-affinity. Oxygen adsorbed on the surface of the grains extracts an e- to ionize into O^- or O_2^- species, which increases the resistance of the sensor coating. Upon exposure to a reducing gas, the adsorbed oxygen species, being exceedingly metastable, oxidize the reducing gas, releasing the trapped electron and consequently lowering the resistance. The amount of resistance change is proportional to the concentration of the reducing gas in the ambient, which is supposed to be the dominant sensing mechanism of surface conductive gas sensors like SnO_2.

The sensor resistance (R) can be written as

$$R=R_0\exp(E_b/kT) \qquad (1)$$

Where, R_o is a constant and E_b is the barrier height. It can be shown that E_b is proportional to the square of the coverage and consequently the conductivity has an exponential dependence on the square of the coverage. The sensitivity of a sensor is calculated from either of the following relations: ……………………………..(2)

$$S = \left(\frac{R_T - R_B}{R_T}\right) \times 100$$

$$S = \frac{R_T}{R_{GAS}} \qquad (3)$$

Where, R_T is the sensor resistance in air at a particular temperature and R_{GAS} is the sensor resistance in gas at the same temperature.

Experimental

Doped ZnO powder sample were prepared by sol-gel technique. Before the precipitation reaction, zinc acetate [$Zn(CH_3COO)_2$] (Merck) was dissolved into de-ionized water, and ammonia was diluted with deionized water to a concentration 1 mol/L. Then the ammonia diluted was dropped into the $Zn(CH_3COO)_2$ solution under continuous stirring, and the pH value of 8. The precipitate was aged for 50 minute, and then filtered, washed with de-ionized water, followed by drying at 373K and sintering at 873K for 1 h, and finally cooled down naturally. In impregnation method doped ZnO were doped with different depends such as Ru, Mg, Pd, Y, La, V, and Na. The compound sources of dopants were magnesium oxalate, ruthenium tri-chloride, iridium tri-chloride, palladium chloride, lanthanum chloride, ammonium meta-vanadate and sodium carbonate, respectively. The amount of dopants was about 2 wt.% based on ZnO for gas sensing materials or catalyst coatings.

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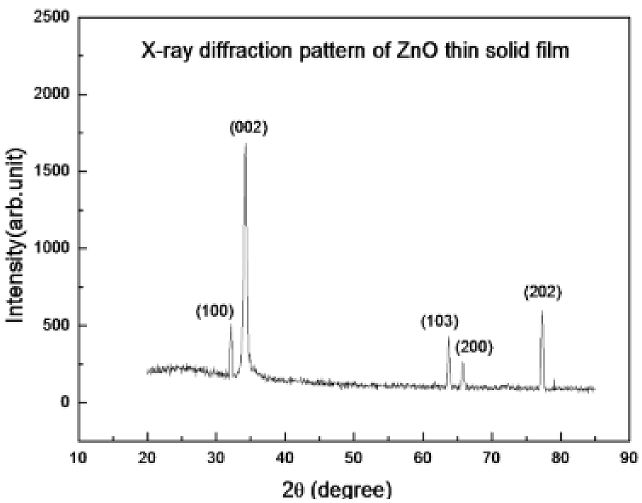
Results and Discussion

Crystal structure of the powder was characterized by X-ray diffractometer with monochromatized Cu K (λ = 1.5418A°) incident radiation.XRD patterns were recorded from 20^{o} to 85^{o} (2θ) .The XRD pattern of 2 wt.% Al–doped ZnO is shown in Fig.2 All the diffraction peaks could be indexed to wurtzite ZnO (JCPDS card No.36-1451, *a* = 0.3249 nm, *c* = 0.5206 nm) with high crystallinity.



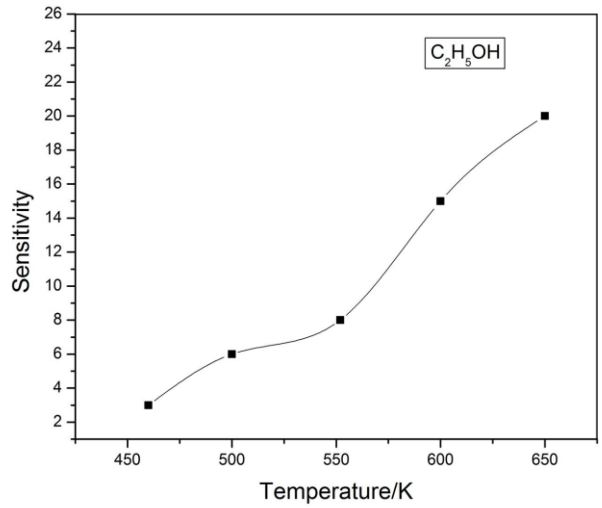


Fig.2 XRD of doped ZnO

Fig.3 Relation between working temperature and responses.

In order to research the gas sensing properties of ZnO-based sensor, in this paper it was observed the responses to gas (C_2H_5OH) in a temperature range of 450-650K.It was observed from the graph shown in Fig.3 that the response of the sensor increased with an increase in working temperature. The alcohol response and the conversion ratio of C_2H_5OH increased with an increase in working temperature, and their changing trends are similar to each other. The response of the ZnO sensor toward C_2H_5OH is dependent on the conversion ratio of C_2H_5OH or formation of CH_3CHO.

It was happened when an n-type semiconductor particle is exposed to air, oxygen molecules can adsorb on the surface of the particle and form $O_2^{\ -}$, O_2^{2-}, O_2^{-} ions by capturing electrons from the conductance band, which in turn produces an electron-depleted space-charge layer in the surface region of the particle [13]. The fewer electrons present in the conduction band lead to a higher surface potential barrier, and therefore, result in a higher resistance [14]. Molecular-type adsorbates (O_2, O_2^{-}), dissociative type one (O_2^{2-}) and surface (lattice) oxygen (O_2^{-}) are confirmed to exist on the surface of an n-type semiconductor particle [15].

In addition, all of these adsorbed oxygen species are discerned to desorb depending on the adsorption conditions. Since gas sensors are usually operated at 573K and above, the $O_2^{\ 2-}$ species is more important than other oxygen adsorbates [16].

The target gas (ethanol) may undergo different reactions,and then can take two routes of decomposition reaction, i.e.,dehydration and dehydrogenation:

$C2H5OH \rightarrow C2H4 + H2O$(acidicoxide) ……………………………..(1)

$2C2H5OH \rightarrow 2CH3CHO + H2$ (basicoxide) ………………………..(2)

These primary products thus formed are consecutively oxidized to CO, CO2 and H2O.

$C2H4 + 3O_2{-}\ (ad) \rightarrow 2CO2 + 2H2O + 6e^{-}$ (3)

$2CH3CHO(ad) + 5O_2^{2-}\ (ad) \rightarrow 4CO2 + 4H2O + 10e^{-}$ (4)

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Since ZnO is a basic oxide, dehydrogenation is favored. The catalytic oxidation of alcohol over ZnO agrees with the above results because only one intermediate product (CH_3CHO) can be detected.

Role of ZnO in Sensing Activity

Many researchers studied the sensing behavior of ZnO nanoparticles, nanorods etc. on LPG gas, H_2S, CO, H_2 and Cl_2. It was observed that ZnO nanoparticles are more sensitive on H_2S as compared to CO, H_2 etc, ZnO nanorods are more sensitive on LPG to N_2 and CO_2. ZnO nanostructure on multilayer graphene shows the response value reached to 35.8 under the exposure of 100 ppm of acetone. Interconnection between ZnO nanoparticles plays better role in gas sensing rather than the influence of surface to volume ratio, and particles size. ZnO nanoparticles can form ionic species on sample surface upon adsorption and desorption of test gas molecules.Response and recovery time are an important parameters for evaluating the sensor potential applications. ZnO nanostructured material shows fast response and recovery in ethanol gas for 50 ppm concentrations. Synthesized ZnO nanoparticles by simple heat treatment method were used as source for thermal evaporation technique to obtain gas sensing characteristics and temperature dependent gas sensing properties are on exposure of host gas (ethanol) a static gas sensing set up. The gas response ($S = R_a/R_g$) of synthesized ZnO towards the host gas was measured. Where R_a is resistance in air and R_g is resistance in the presence of gas. ZnO based sensor can sense the environment changes, due to adsorption (surface defect) and desorption of test gas molecules. ZnO nanoparticle sensor has strong chemical affinity during heating for specific gas molecules. Before exposure to host gas, oxygen atoms are adsorbed into ZnO surface; it takes electrons from surface and become O^- (release oxygen). This O^- ion helps to create the depletion layer on the host surface. This allows more oxygen to be adsorbed, and in this way sensing response are detected.

Importance of Ethanol Sensor

In case of safety on the road as well as in the workplace it is necessary to detection of alcohol concentration in the brain is important. Expediently, blood alcohol concentration (BAC), defined as the percentage of alcohol in the blood, is used to assess the alcohol level in the brain tissue as a measure of impairment from alcohol poisoning [17]. Most people demonstrate the measurable mental impairment at about 0.05 % BAC. Above this level, the ability to operate an auto-mobile deteriorates progressively with increased blood alcohol level. For the average person, unconsciousness results at about a BAC of 0.4 %.Above 0.5 % BAC, basic body functions such as breathing or the beating action of the heart can be depressed that causes death. Another challenging need of alcohol detection is in the area of automatic control of fermentation processes, especially when alcoholic fermentation needs to be avoided.

Conclusion

The lack of a centre of symmetry in wurtzite, combined with large electromechanical coupling, results in strong piezoelectric and pyroelectric properties and the consequent use of ZnO in mechanical actuators and piezoelectric sensors. Also ZnO is transparent to visible light region. The change of conductivity at the present of reducing gases makes them suitable material for gas sensors. The ethanol sensing property of ZnO creates a great scope for developing a low concentration ethanol sensor.

Much effort is being made to extend the working temperature range of metal-oxide gas sensors and lower the optimal working temperature. The goal of these investigations is to decrease the power consumption of sensor elements.

The problem of sensor stability deserves more attention than it has now. Higher stability will decrease the frequency of or completely eliminate the need for verification and re-calibration of sensors. Another important problem is the development of simpler sensor materials and cheaper preparation methods.

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