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Influence of the Lanthanum Doping on the Gas Sensing Properties of the Magnetron Sputtered ZnO films for H_2O_2 Vapor Detection

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Abstract. This study presents the fabrication of a high-performance hydrogen peroxide vapor sensor based on ZnO film doped with different concentration of La using the high-frequency magnetron sputtering method. The responses (R_{gas}/R_{air}) of the fabricated sensors were measured at various operating temperature to different concentrations of hydrogen peroxide vapors. Gas sensing tests indicate that the maximum sensitivity was observed for 2 at.% La concentration in ZnO material and sensor exhibit high sensitivity to low concentration of hydrogen peroxide vapor. We expect that in the future, ZnO doped with 2 at.% La sensitive films will be able to be utilized in highly sensitive, real-time hydrogen peroxide vapor sensors.

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Keywords: zinc oxide, conductometric sensor, magnetron sputtering, hydrogen peroxide vapor, sensitivity

1. Introduction

In modern time, detecting of undesirable chemical or biochemical forms has gotten to be significant research and various gas sensors have been fabricated and functioned in natural monitoring, human security, medical applications, and industrial automobiles applications. Today, hydrogen peroxide vapor is considered to be a useful substance, which is used in pharmacy, medicine, industry, agriculture and household. Subsequently, it is exceedingly desirable to create a reliable sensor that can successfully identify H_2O_2 indeed with amazingly low concentration [1-4].

Semiconductor gas sensors (conductometric) based on metal oxide semiconductor (MOS) have incredible potential for commercial application in natural monitoring and healthcare due to the properties low cost, easy to miniaturize and production, high stability, selectivity, sensitivity, reliability, fast response, low control utilization, long lifetime, and the capacity to operate in cruel situations. In the manufacturing of conductomertric gas sensors, several types of MOS materials have been explored, including SnO_2, ZnO, In_2O_3, TiO_2, WO_3, CuO, and Fe_2O_3 with different dopants and morphologies [5-8].

1.1 The properties of ZnO material

Among the oxides, ZnO has some advantages such as its low cost, wide bandgap energy (3.4 eV), simple synthesis of nanostructures, high mobility of electron carriers, large exciton binding energy (60 meV) at room temperature and non-toxicity in nature that makes it eco-friendly. Zinc oxide is a group II–VI compound semiconductor and has promising catalytic, electrical, electronic, and optical properties. It has recently attracted great attention due to its physical properties and potential applications in solar cells, gas sensors and other electronic nanodevices.

Zinc oxide is one of the most studied MOS materials due to its unique surface properties. ZnO has crystal structures of wurtzite, zinc blende and rock salt. The wurtzite is the most thermodynamically and chemically stable phase structure under ambient conditions. The wurtzite structure is a hexagonal close-packed structure (Fig. 1). Table 1 lists the main physical and chemical properties of ZnO material [9, 10].

Understanding the fundamental physical and chemical properties is the best way to the rational design of functional devices. In study of the properties of ZnO nanostructured material is essential for developing their potential as the building blocks for future nanoscale devices. The monocrystalline and polycrystalline (small grains with diameter of 15-30 nm) ZnO structures show a superior fatigue resistance, high isoelectric point and charge transfer properties, biocompatibility, and low impact on the environment at the end of life cycle. ZnO based nanomaterials are easy to fabricate, and raw materials and precursors are easily available [11].

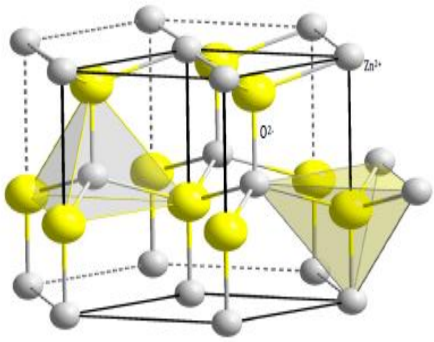

Fig. 1. The wurtzite structure of ZnO [12].

This material is also widely used in various gas sensors as a high-sensitive material with combination of 3 S parameters (Sensitivity, Selectivity and Stability). In particular, the polycrystalline structure of this material has quite promising parameters in terms of use in gas sensors. Due to its high chemical stability, catalytic activity and large surface area to volume ratio, ZnO polycrystalline material has become one of the main materials used in gas sensors [13].

Table 1. The physical and chemical properties of wurtzite ZnO.

Properties	Value
Lattice constants (T = 300 K)	
a_0	0.32469 nm
c_0	0.52069 nm
Density	5.606 g/cm^3
Melting point	2248 K
Relative dielectric constant	8.66
Gap Energy	3.4 eV, direct
Intrinsic carrier concentration	$<10^6$ cm^{-3}
Exciton binding energy	60 meV
Electron effective mass	0.24
Electron mobility (T = 300 K)	200 cm^2/Vs
Hole effective mass	0.59
Hole mobility (T = 300 K)	5–50 cm^2/Vs
Molar mass	81.406 g/mol
Heat capacity (C)	40.3 K^{-1}mol^{-1}
Gibbs free energy ($\Delta_f G^\circ$)	-320.5 kJ mol^{-1}

Although pure ZnO has not represented high sensing performance but conductometric sensors based on doped ZnO nanostructured material exhibit high sensitivity, selectivity and stability toward both oxidizing and reducing gases. As an excellent dopant, lanthanum oxide (La_2O_3) is considered a material as a conductometric type gas sensor for sensing a large number of gases [14-18].

In this study, we prepared La doped ZnO based sensor for detection of hydrogen peroxide vapor and confirmed the influence of the lanthanum doping on the gas sensing properties by means of gas sensing studies.

2. Experimental

The sensitive layers were deposited by magnetron sputtering method. First, sputtering targets (5 targets) based on ZnO (wurtzite) doped with 0.5; 1; 1.5; 2; 2.5 at.% La_2O_3 were fabricated using solid-phase reaction method. The process used to prepare the magnetron sputtering targets may be found in our previous reports [19]. The synthesized ZnO<La> compositions were subjected to mechanical processing in order to eliminate surface defects having smooth, parallel tablets with the diameter of 50 mm and the thickness of 2 mm.

Magnetron sputtering is one of the best methods for obtaining thin films from very wide range of materials including metals, dielectrics, ceramics, polymers and so on [20, 21]. Magnetron sputtering is a process whereby atoms of a solid target material are ejected (or vaporized) due to the momentum transfer from an atomic-sized energetic bombarding particle impinging on the target surface. Then these vaporized particles are condensed on the substrate material. The sputtering is carried out using gaseous ions from plasma that are then accelerated and directed toward the target. The plasma used during the sputtering is created and controlled by magnetron guns [22].

The ZnO<La> sensitive layers were deposited by the VTC-600-2HD DC/RF Dual-Head High Vacuum Magnetron Plasma System [23]. As known, plasma is weakly ionized quasi-neutral gas made up of ions and electrons to be a good electrical conductor. Generally, processes that depend on the use of the plasma are referred to as plasma processing. The plasma processing has plasma densities between 10^8~10^{13}/cm^3 and during the sputtering of the ZnO<La> layer the plasma density was 10^{10}/cm^3. The gas atoms may not be fully ionized and there are not only electrons and ions but also neutrals. The electron velocities are much higher than that of ions and neutrals. The plasma properties are heavily dependent on the excitation and ionization energies of the gas. The most suitable gas is argon (Ar) because it is an 'inert' or 'noble' gas, thus not explosive when subjected to the RF (13.56 MHz) magnetic field or spark and it has low ionization energy (15.7 eV). High purity argon (99.99%) was used as a plasma sustaining gas during the sputtering of ZnO<La> targets obtaining gas-sensitive film with enhanced parameters. The krypton gas is also a good candidate for this application, but it's expensive. Ar is relatively cheap to manufacture since it is extracted directly from the atmosphere [24]. Generally, plasma can be used for different purposes depending on the type of the PVD process. It can be used as a source of ions or as a source of electrons. For applying power sources for discharge there are two sources: DC (continuous DC, Pulsed DC) and AC (LF (~100 Hz), MF (~100 Hz - ~1 MHz) and RF (> ~1 MHz)). The RF magnetic field with 13.56 MHz was used by us as a power source. For magnetron DC and AC sputtering processes plasma is used as a source of ions for the sputtering from a target material if the plasma ions are directed toward it. The uniformity of plasma is very important concern for more tunable deposition process environment. Plasma uniformity is mainly dependent on sputtering system geometry and the means by which the plasma was produced. The plasma produced by DC diode is not ideal for sputtering because the electrons ejected from the cathode are accelerated away from the cathode area and are not efficiently used for sustaining the discharge [25].

Ceramic substrates with the interdigitated electrodes, the temperature sensor (Pt 1000) and the heater were used as sensor substrate (Multi-Sensor-Platform) [19]. Gas sensitive ZnO<La> layers were deposited onto Multi-Sensor-Platform by the VTC-600-2HD DC/RF Dual-Head High Vacuum

Magnetron Plasma System under the following conditions: 60 W input power, 150 °C deposition temperature, 70 mm distance between the target and substrate, 2×10^4 Pa base pressure, 6×10^{-1} Pa deposition pressure, and 15 minutes duration of sputtering. Then, the sensors were sensitized by deposition of palladium catalytic particles on the surface of the sensing layers by the ion-beam sputtering method (the deposition time was 3 seconds, the cathode current and the anode voltage were equal to 65 A and 25 V, respectively). Finally, the samples were annealed at 350 ^{0}C during 3 hours for stabilization of sensing parameters. Five different sensors (from targets of ZnO doped with 0.5; 1; 1.5; 2; 2.5 at.% La) were made with the same technological modes described above.

It should be noted that the deposition rate of RF magnetron sputtering was almost unaffected by the percentage of dopant in the ZnO material. The films deposited in the same technological modes from all 5 targets had almost the same thicknesses (80 nm).

3. Results and Discussion

The gas sensing properties of the ZnO<La> thin layers were studied in the presence of hydrogen peroxide vapors using a home-made computer-controlled gas testing system [18]. To have the necessary concentration of H_2O_2 in the chamber, the liquid hydrogen peroxide was introduced into the chamber on the special hot plate designed for the quick conversion of the liquid H_2O_2 to the gas phase. The response of the fabricated sensors is calculated as, $R=R_{gas}/R_{air}$, where R_{air} is the resistance of the sensor in the presence of air and R_{gas} is the resistance in the presence of the target gas.

At first, the sensing responses of the ZnO<1at.% La> film at 150 ^{0}C operating temperature towards ppm level of H_2O_2 were tested and the results are shown in Fig. 2 (as a structure prepared for pre-testing). The results indicated that the sensor exhibited clear and reversible gas responses to ppm levels of the gas. The absolute sensor responses to H_2O_2 vapors at the concentrations of 100 and 200 ppm, were about 3 and 14, respectively.

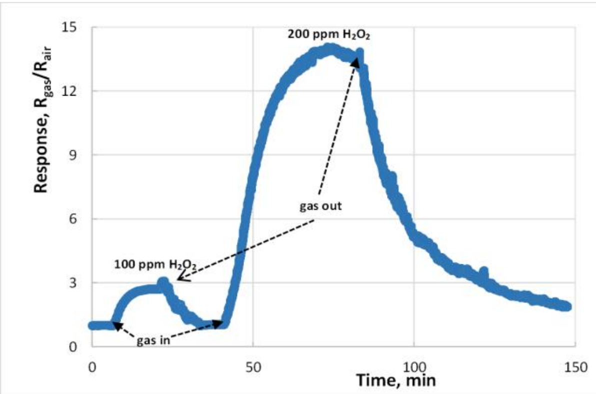

Fig. 2. The response-recovery curves of ZnO<1at.% La> sensor observed at different concentration of H_2O_2 vapors at 150 ^{0}C operating temperature.

The gas-sensitive properties of the sensors based on ZnO doped with 0.5; 1.5; 2; and 2.5 at.% La were also studied. A change in the concentration of the dopant in the ZnO material changes its resistance, but the dependence has no pattern (Fig. 3). It is assumed, that such behavior is associated with stoichiometric disorders of the thin film ZnO. The minimum resistance (0.07 MOhm) is observed in the case of 0.5 at.% concentration of La and the maximum (25.6 MOhm) in the case of 2.5 at.% La.

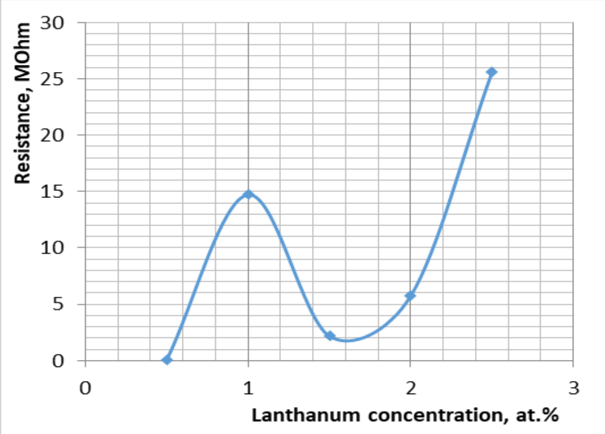

Fig. 3. The dependence of the ZnO<La> sensor's resistance on the lanthanum concentration at 150 ^{0}C operating temperature in the air.

The response-recovery curves of ZnO<La> sensor with different percentage of La observed at 100 ppm of H_2O_2 vapors at 150 ^{0}C operating temperature are presented in Fig. 4. The maximum sensitivity was observed at 2 at.% La concentration in ZnO material and increased concentration of the dopant has led to a sharp drop in the response (Fig. 5).

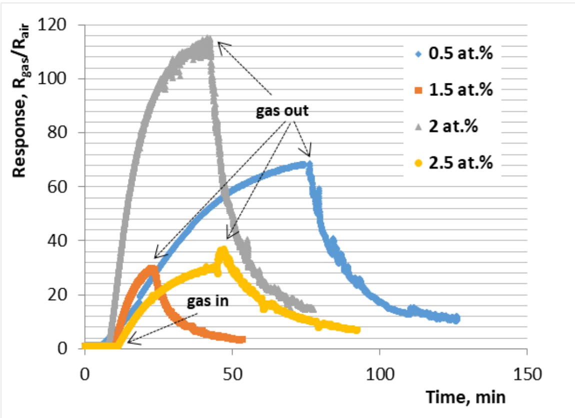

Fig. 4. The response-recovery curves of ZnO<La> sensor with different percentage of dopant (La) observed at 100 ppm of H_2O_2 vapors at 150 ^{0}C operating temperature.

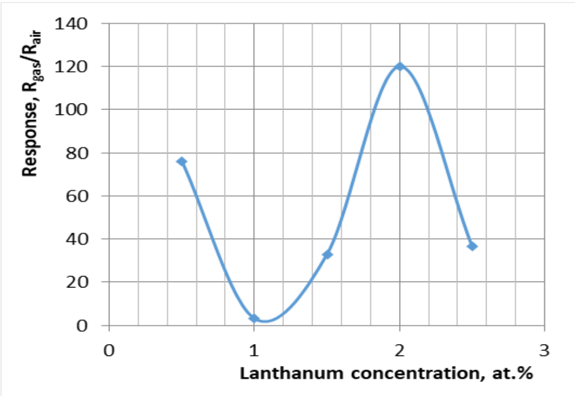

Fig. 5. The dependence of the ZnO<La> sensor's response on the lanthanum concentration in the presence of 100 ppm H_2O_2 vapors at 150 ^{0}C operating temperature.

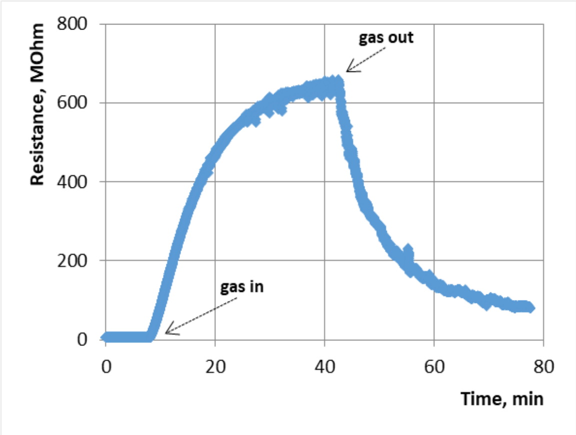

Fig. 6. The resistance variation of the ZnO<2 at.% La> sensor in the presence of 100 ppm hydrogen peroxide vapors at 150 °C operating temperature.

This ZnO<2 at.% La> based sensor showed extremely high sensitivity to very low concentrations of hydrogen peroxide vapors at relatively low operating temperatures. The resistance variation of the ZnO<2 at.% La> sensor in the presence of 100 ppm hydrogen peroxide vapors at 150 °C operating temperature is presented in Fig. 6. At this concentration of H_2O_2, the resistance of the film changes more than 120 times and after eliminating the effect of target gas, the resistance is almost completely recovered.

4. Conclusions

The La doped ZnO sensitive thin films were successfully prepared and demonstrated hydrogen peroxide vapor sensors at low operating temperature. The excellent gas sensing performance can be attributed to the following aspects: among the introduced concentration of La in ZnO (0.5; 1; 1.5; 2; and 2.5 at.%) the ZnO doped with 2at.% La sensor provides not only high response to ppm level of H_2O_2 vapors at low operating temperature but also fast response and recovery behavior at the presence of hydrogen peroxide vapor. To introduce optimum amount of La_2O_3 dopant into the ZnO base material can be maximized and present best sensing properties.

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