Structural, Optical, Electrical and Gas Sensor Properties of ZrO_2 Thin Films prepared by Sol-Gel Technique

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Abstract

Sol-gel deposition technique has many advantages to synthesis nano-oxide thin films. Surface morphology and structural properties of the film depend on the doping and solvent solution used with optimal parameters. The ratio of surface to volume is positive for the gas senor. Zirconium oxide can be considered a remarkable material and this attributed to its superb mechanical, biological and optical characteristics. For this reason, five different samples of Zirconium oxide thin films were deposited by the sol-gel technique with numerous molarities (0.25, 0.05, 0.075, 0.1 and 0.125M). The XRD technique shows that there are two phases, one of them is tetragonal Zirconia (t-ZrO_2) and the other one is monoclinic Zirconia (m-ZrO_2). The increment in tetragonal phase has been occurring at high molarities of the solution. ZrO_2 thin film crystalline size increases with increasing solution molarities. UV-Vis spectra reveal that ZrO_2 thin film has transmission value higher than 70%. Finally, the sensor measurements show that fast response (4s) and quick recovery time (10s).

Key Words: Zirconia Thin Films, SOL-GEL, Ammonia Gas SND Gas Sensor.

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Introduction

Zirconia thin films are of great interesting due to their inevitable applications in different fields such as biological and optical fields [1]. Thin films of metal oxide, like ZrO_2, TiO_2 and AlO_2 is an important for optical applications such as antireflective coatings, protective layers and microelectronic devices[2]. Zirconium dioxide in an inclusive condition has three crystal structure (Cubic "c", Tetragonal "t" and Monoclinic "m"), all these phases are thermodynamically stable at different temperatures range. ZrO_2 has a stable monoclinic structure with temperature below 1170°C. The tetragonal phase thermodynamically stable at range (1172-2370°C), and cubic structure stable above 2370°C. Due to the high dielectric constant of Zirconia, it is good material can be utilized as a suitable substitute of silica for the dielectric gate in the manufacturing of CMOS. Zirconia features amazing properties such as a high-dielectric constant, broad band gap, thermal stability and high refractive index [3,4]. ZrO_2 thin film can absorbs photon by two inter band transitions (direct and indirect transition at 5.87eV and 5.22eV, respectively) [5]. ZrO_2 applications may be increment by a number of methods (calcination, doping and molarity variation etc.) [6]. Because of the pale white color of Zirconia, it's useful material for aesthetic farming and it acts an important role in dental materials, like implanted teeth[7,8]. Zirconia thin film prepared by different mechanics, like sol-gel, spray pyrolysis and laser ablation and others [9].

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Spray pyrolysis and sol-gel methods are widely used because of its low cost[10]. Thin film thickness can be change in sol-gel technique by increasing the molarity and the number of solution droplets [11]. In this article, Zirconium oxide thin films were prepared by sol-gel technique at various molarities. The structural properties, optical properties, electrical conductivity and the sensitivity of this detector to ammonia gas were studied.

Experimental Detail

$ZrOCl_2.8H_2O$ with impurity 99.99%, which utilized as a source of zirconium with deionized water. It was blended with deionized water and stirred until obtained transparent and shiny solution. Various molarities of solution were prepared (0.025, 0.050, 0.075, 0.1 and 0.125M). The solution of zirconium oxide was spinning at 1000rpm on the substrate of glass for 15sec and annealed at 350 °C for 2h. Acetone and isopropyl alcohol were used to clean glass substrates. Shimadzu 6000 instrument XRD with λ=1.5045 Å was depend to evaluate the structural properties of the ZrO_2 thin films. Shimadzu UV-140 was used to study optical properties. The electrical circuit "sensitive digital electrometer type Keithley (616) and electrical oven" was used to measure the electrical conductivity as a function of temperature for thin films in the range (R.T – 200)°C. Gas sensor for ammonia effect on films which test by using a homemade machine.

Result and Discussion

1) X-ray Diffraction (XRD)

X-ray data of ZrO_2 thin films have been shown in Fig.1, there are two phases was observed, tetragonal "t" and monoclinic "m". Peaks at 28.1° , 31.4° and 45.5° correspond to $(11\bar{1})$, (111) and $(20\bar{2})$ planes of monoclinic structure (m-ZrO_2) [JCPDS card no. 13-307]. While peaks at 54.3°, 56.8º, 66.7º, and 76.6° at (220), (113), (231) and (330) planes represent tetragonal structure (t-ZrO_2) [JCPDS card no. 17-923]. Debye Scherer's formula eq. 1 was used to calculate crystallite size of Zirconia.

$$D = \frac{k\,\lambda}{\beta \cos\theta} \quad \text{.................................} (1)$$

Where D: the crystalline size of the prepared sample, λ is the x-ray wavelength and θ is the Bragg's angle, B is the full width at half maximum of a Bragg's peak.

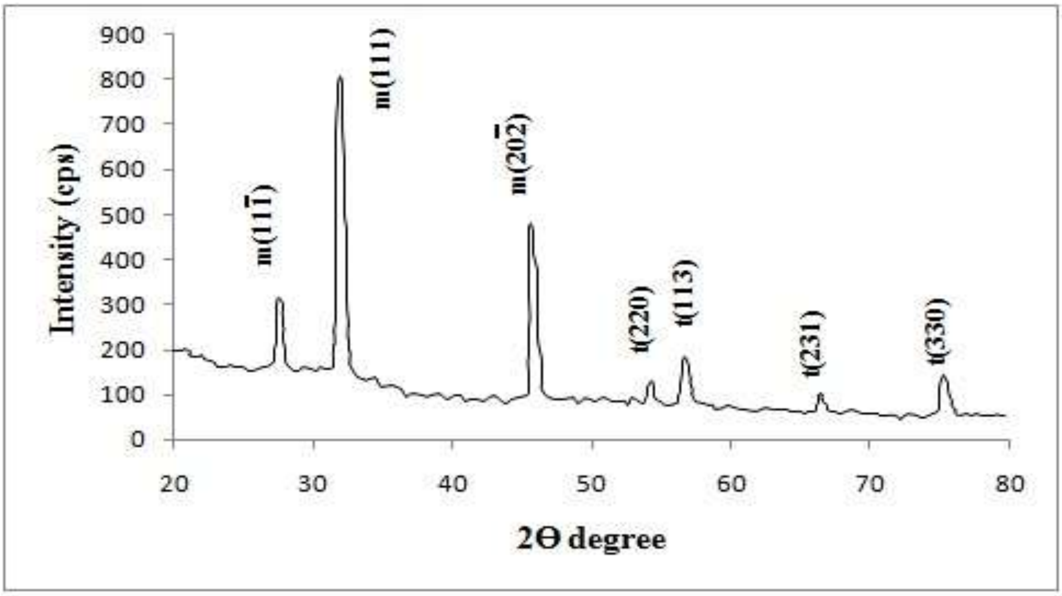

Fig. 1. X-ray diffraction peaks of ZrO_2 thin film prepared with 0.125 M

Fig.2 shows the Zirconia crystallite size, which determined at a strongest peak (111) for a monoclinic phase, an increase in a solution morality was lead to increases in a crystallite size of ZrO_2 films, this occurred because there are more dissolved atoms to interact with each other and this leading to a strong bonding between atoms and largest crystallite size. At high molarities, it was observed a slight displacement in the peaks towards lower angles and this attributed to existence of a stresses in ZrO_2 films.

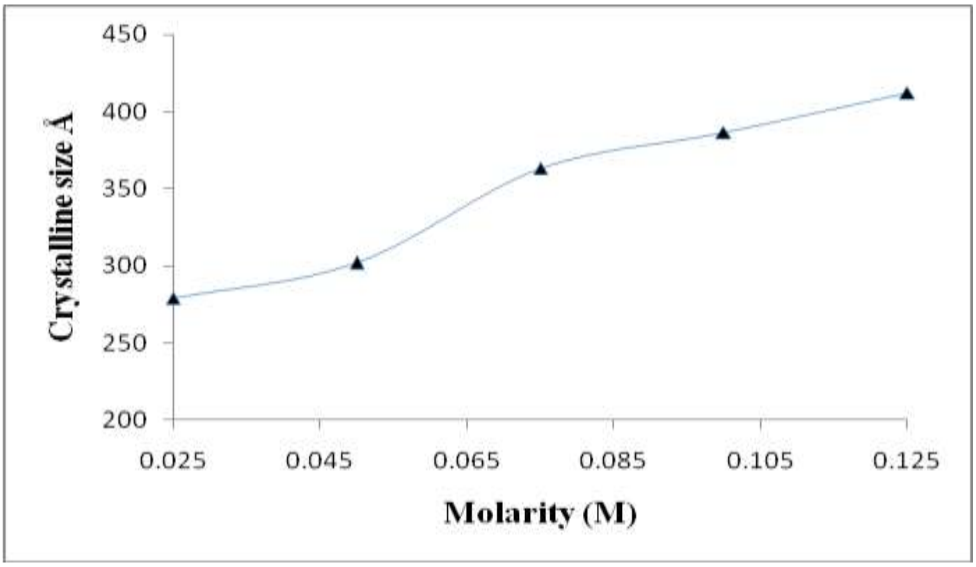

Fig.2. Crystalline size of ZrO_2 thin films as a function of molarity

The volume of the unit cell and x-ray density of Zirconium oxide thin films was determined by equations (2 ,3 and 4) [12] and is plotted as shown in Fig.3

$$V_{monoclinic} = abc \sin\beta \quad (2)$$

$$V_{Tetragonal} = a^2 b \quad (3)$$

$$\rho = \frac{1.66042 \sum A}{V} \quad (4)$$

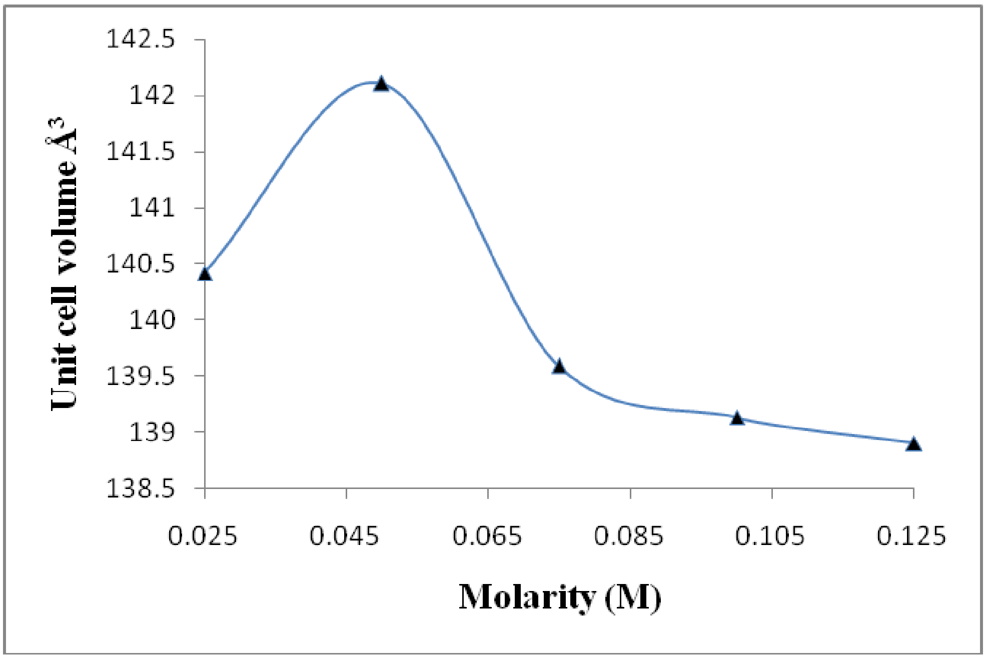

Fig.3. The volume of the unit cell of ZrO_2 thin film as a function of molarity

Fig. 3 show an increment in volume of the unit cell up to 0.050 morality and decrement after this value, this turn contributes to convert the phase from monoclinic to tetragonal. The reduction in the volume of a unit cell is attributed to the small reduction in the lattice parameters in both (m-ZrO_2 and t-ZrO_2) phases. The decrement in the unit cell volume and contraction in the lattice parameters can attributed to the higher relative value of the density of x-ray as shown in Fig.4.

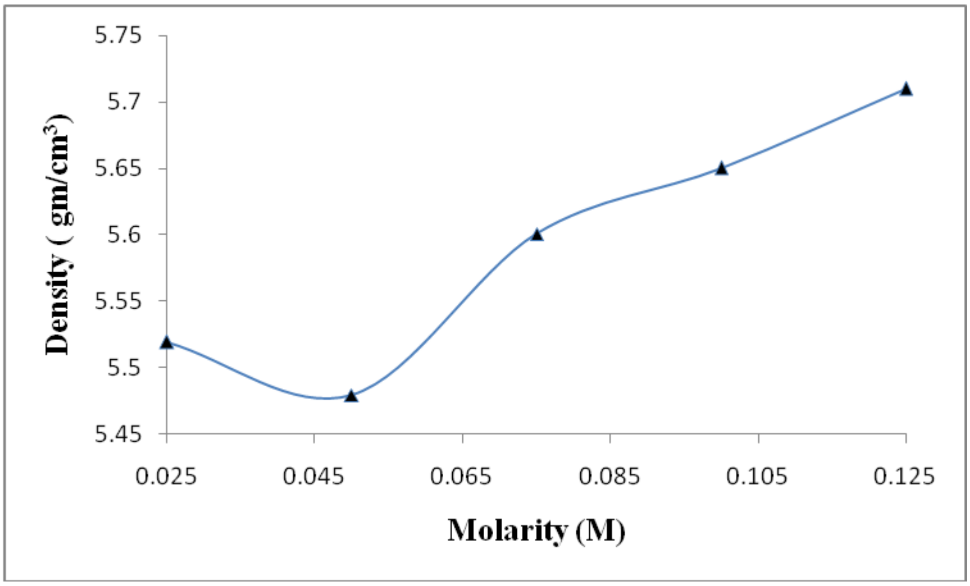

Fig. 4. ZrO_2 thin films density as a function of molarity

2) UV-Vis Measurements

Fig.5 reveals the transmittance spectrum of ZrO_2 thin films at (0.1 and 0.125)M with a wavelength range of (200 to 800)nm. From this figure, it was observed the transmission is within the visible region and reach up to 70%.

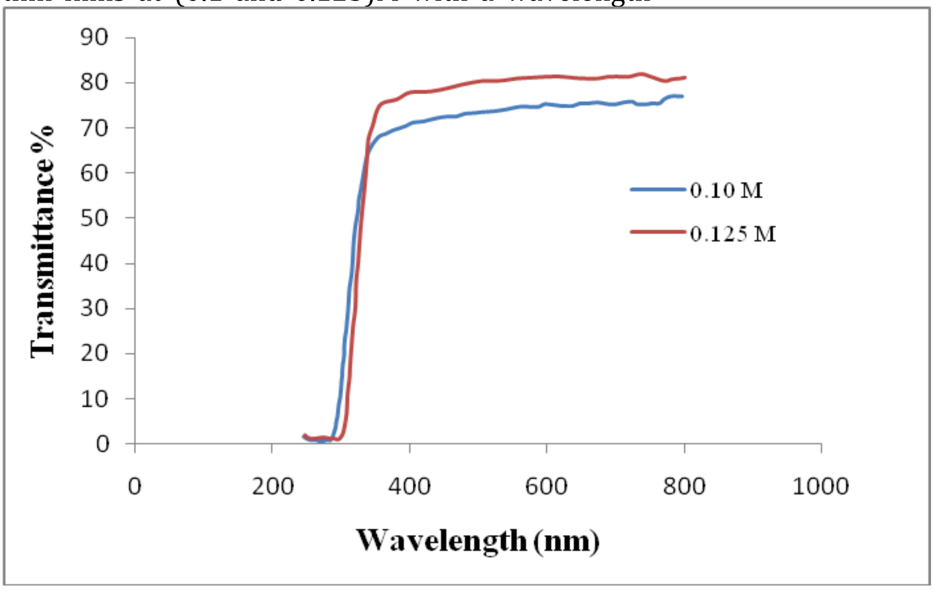

Fig. 5. Transmittance spectra of ZrO_2 thin films at 0.10M and 0.125M

3) Electrical Properties

The variation of conductivity vs. the temperature was shown in Fig.6. The elec-trical conductivity (equ.5) of ZrO_2 thin films varies linearly with temperature. The conductivity was increased with an increment in temperature attributable to the semiconducting nature and negative temperature coefficient of the thin films resistance. This attributed to the propagation of electrons by thermal excitation [13].

$$\sigma = \sigma_o \, e^{(-\frac{\Delta E}{KT})} \quad \text{.................(5)}$$

Where σ is conducted, σ_o is conductivity constant, T is temperature and k is Boltzmann constant.
The conductivity of thin film at 0.125 M was higher than 0.1 M due to increase carrier concentration with molarity increase.

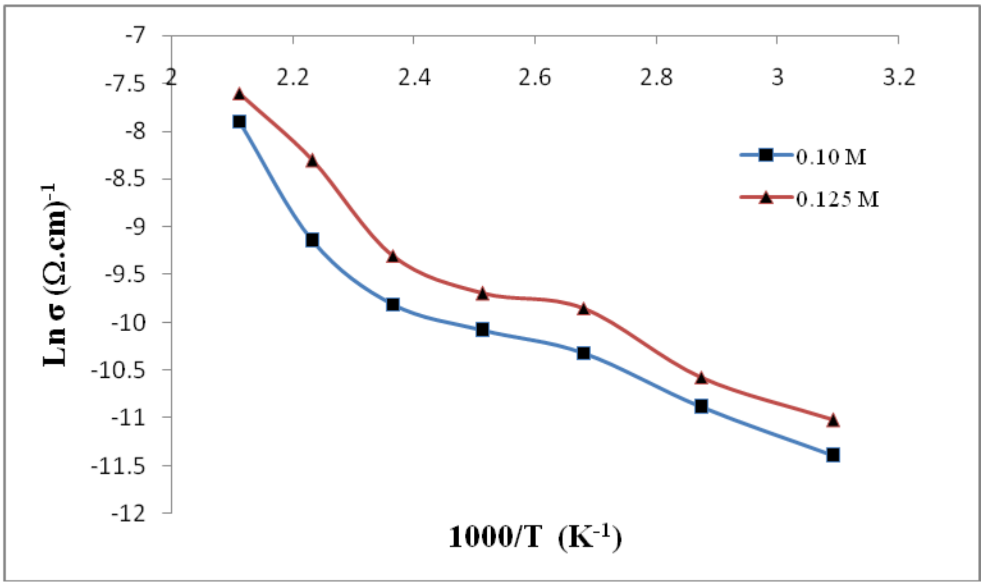

Fig. 6. ZrO_2 thin film electrical conductivity at 0.10 and 0.125 M

4) Gas Sensor Characteristics

The gas response of the thin film (S) is defined as the ratio between the change in conduction of the thin film in gas (G_g) to the conduction of thin film in air (G_a) [13`].

$$S = \frac{G_g - G_a}{G_a} \quad \text{.................(6)}$$

Fig.7 can show the variation between gas response and operation temperature of ZrO_2 thin film (0.10 M and 0.125 M) when 500ppm ammonia is exposed. From this figure it's clear that the thin film response to ammonia at 0.125M (S=60%) is higher than its response to 0.10M (S=20%) at 100°C.

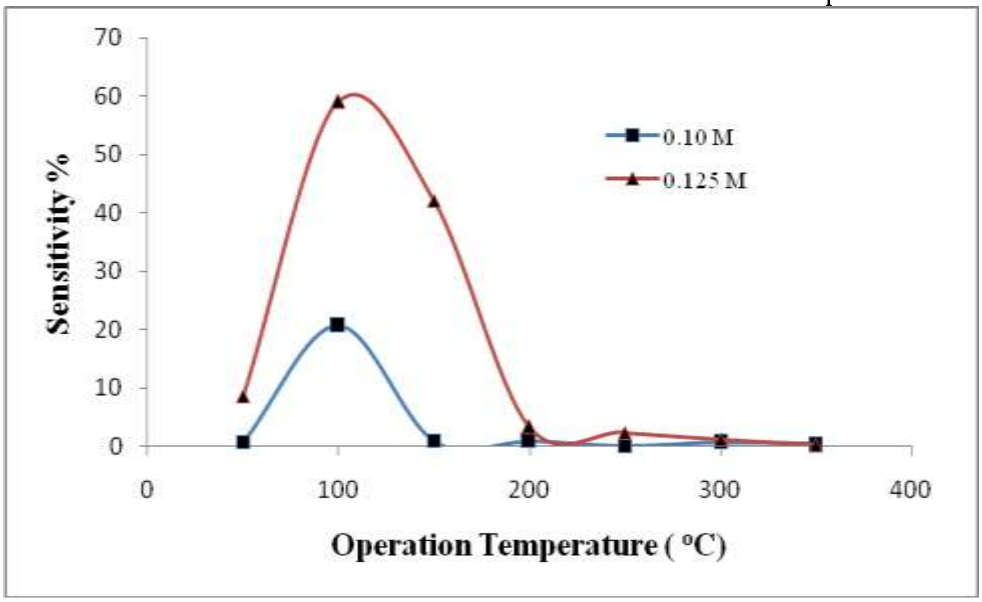

Fig.7. Sensitivity of ZrO_2 thin films to ammonia gas

5) Response and Recovery Time

The response time is define as the time required for the thin film to reach 90% of the low resistance when contact with gas. While the time takes to get back 90% of the resistance is called the recovery time.

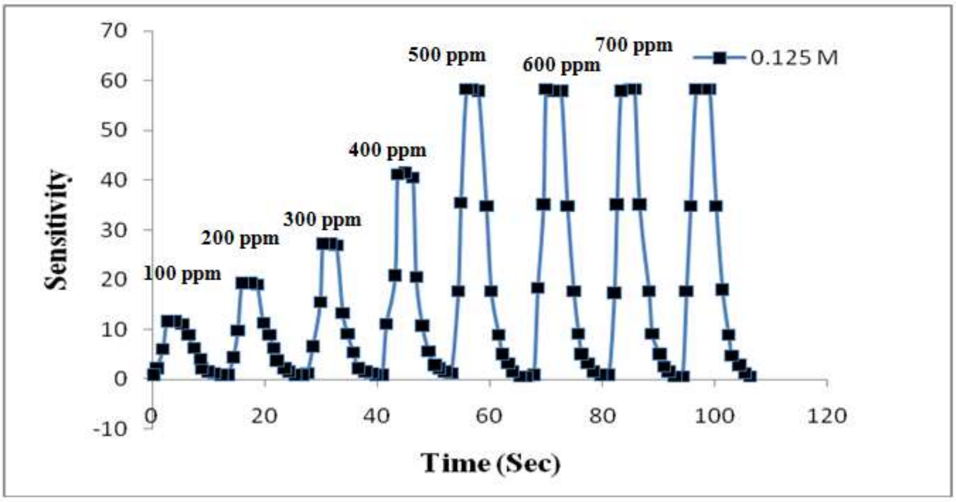

Fig. 8. Response and recovery of the ZrO_2 thin film at 0.125 M

Conclusions

1. In this article, ZrO_2 films were prepared using a sol-gel technique. Like a primary material and molarity in the starting solution, Zirconyal chloride octa hydrate was used to prepare thin film with different molarities.
2. X- ray diffraction peaks show the formation of both monoclinic and tetragonal ZrO_2 phases, and the crystalline size of ZrO_2 thin films increased with an increase in the molarity of the solution.
3. Transmission spectrum showed a high value of transmitting up to 70%.
4. Thin film conductivity at 0.125M was higher than at 0.1M.
5. It was noticed that the fast response time (4s) and fast recovery time (10 s).

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In this article, ZrO2 films were prepared using a sol-gel technique. As a primary material and molarity in the starting solution, Zirconyal chloride octa hydrate was used varing from 0.025 to 0.125M.

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