Synthesis of ZnO: Al thin films Deposited on Porous Silicon for CO Gas Sensing

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Abstract. Porous silicon (PS) used as a substrate for thin films of pure zinc oxide and ZnO:Al for tow type of (PS): n and p, prepared approximately 450°C by using technique of Spray Pyrolysis(SP) by heat deposition for different doping of with thickness equal to (150 nm). Where the bandgap of energy for the (PS) substrate can calculate by the electrons pumping using Photoluminuce, which it was equal to 2.397 eV. Morphology of up view side of the deposited thin films on the n and p-type of the (PS) has been studied by SEM, AFM, and TEM. The sensitivity of the ZnO pure and ZnO: Al for the prepared thin films for CO gas has been calculated, which it was increased with the rise of concentrations of doping by aluminum, where the sensitivity of n-type of porous silicon is larger than p-type of porous silicon substrate.

Keywords. Aluminum; ZnO; PS; CO; Gas sensing.

1. Introduction
The thin films gas sensors defined as a sensors of solid state kind of sensors, this sensitivity element is consists of generally metal oxide of the semiconductor. Constituents like (SnO2), (ZnO), (TiO2), and (WO 3) have been usually studied by investigators [1]. Among the semiconducting metal oxides, ZnO has been intensely studied for the detection of different gases, such as (H2, CO, NH3, NO2, and ethanol vapors) [2]. The characteristics of high mobility and conductivity in addition that decent transparency for photons, energy band gap (3.32 – 3.27 eV), big exciton compulsory energy (60 meV), and easiness of increasing it in the structures procedure thru ZnO appropriate for optoelectronics, transparent electronics, sensing, light-emitting diodes, lasers diodes, photodetectors [3]. Several inquiries have focused on transitional metals doped II-VI compound semiconductor ZnO, Porous Silicon is not a new material, but it is only recently under research due to its fantastic properties [4]. PS was employed for dielectric isolation of active Si devices [5]. PS has involved a unlimited treaty of attention due to effective R.T. visible light photoluminescence [6].

Lehman and Goesele reported in 1991 that porous silicon manifest that the bandgap increase compared with bulk Si. The bandgap increase explains the observed visible luminescence from porous Si [5, 7]. The principle contrivance for gas recognition by sensors of metal oxides in ambient air is the ion sorption of oxygen of the molecules component at its surface of the thin films, which products a reduction thin layer, (for n-type semi-conductors), and henceforth decreases the conductivity of the films [8]. Ions sorption made used to the process where the variety of adsorption and experiences a delocalized electric charge which removal with the metal oxide of the thin films. Which used for measuring oxidation and reduction for gases, as well as, they would alteration the quantity of ions sorbed oxygen and then the conductivity of the metallic oxide [9, 10]. Captivating the interpretation that identifying reaction takes place mostly on the layer of the sensors external, the controller of semiconductor particle
size will be one of the original necessities for improving the sensitivity of the sensors [11]. The probable for a detonation of a flammable hydrogen with air combination is so high. The smallest temperature of a warm exterior that can burn an inflammable mix, is for H2 within the range between (800-1000) K reliant with the investigational environments. It is comparatively great, then canister be dropped by catalytic shells. H2 gas does not have a minefield as it is previously a gas at ambient environments. It means that cryogenic H2 will flash at all temperatures overhead its boiling point of 293°C [12].

2. Experimental

Each of n-type and p-type of the used silicon were the resistivity within the limited between \(\rho = 0.05 - 0.1 \ \Omega \cdot \text{cm}\) for the (111) orientation of the unit cell, which laboring as \((2 \times 2\text{cm}^2)\) substrate for thickness is about (500 μm) used to synthesize Porous Silicon using the \((\text{PECE})\). The doping concentration of the solution was equal to (0.075M) which using the nitrate of zinc component \((\text{Zn(NO}_3\text{)}_2 \cdot 6\text{H}_2\text{O})\) with M.W. equal \((297.4 \ \text{g/mole})\) melted in purified water. After this used aluminum nitrate \((\text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O})\) of 99.9% purity and molecular weight \((375.13 \ \text{g/mole})\) for doped with Zinc Oxide films. The spray pyrolysis substrate with \((450 \pm 10 \ ^\circ \text{C})\) temperature during the deposition. Where the molarity concentration and the time of solution spray on the heat porous silicon getting different thicknesses of films 3. The period from another spray seconds through the test and stopping for a few seconds (approximately 42 seconds) which was sufficient to arrival the porous silicon substrate temperature. The regulated distance between the nozzle of spray and the porous silicon substrate is 28cm approximately, n and p-type of the thin films are prepared by using \((2, 4, 6 \text{ and } 8) \ %\) of aluminum doping concentration and pure ZnO. The discount principal to the construction of pure ZnO as in this analysis equation:

\[
2\text{Zn(NO}_3\text{)}_2 \rightarrow 2\text{ZnO} \downarrow + 4\text{NO}_2 \uparrow + \text{O}_2 \uparrow \ldots (1)
\]

The process of porous silicon makes from n and p-type silicon can be obtained by photochemical etching, which can make it by a photons of normal white light. Each process can be described as an easy method and as a simple system. The arrangement contained of white light source of \((100W)\) approximately, Hydrogen Florid (HF) solution in ampule made by as cleared in the figure (1). The uniform layer of the porous silicon made several widths which conformed by etching (ECE) and photoelectrochemical etching (PECE). Porous silicon width of many components were manufactured by white light of halogen lamp with PECE method of silicon. Layer of PS manufactured prepared by \((\text{ECE})\) and \((\text{PECE})\) can made by applied 30 mA for approximately a half hour.

Figure 1. (a) Electro-Chemical Etching (ECE) set-up and (b) Photo Electro-Chemical Etching (PECE) cell set-up.

Figure 2 shows optical photographs to the samples of n-type and p-type porous silicon before and after deposition thin films of ZnO and ZnO with different concentrations doped with Al, different colors of samples n-type and p-type is unrecognizable after deposition of the thin films.
3. Results and discussion

3.1. PL Properties
Figure (3) shows Porous Silicon (PS) layers, which be formed on (111) orientations p-type region with using the xenon lamps with (λ=325 nm) at room temperature.

![Figure 3. PL spectra of PS layers formed on p-type regions with (111) orientations at RT.](image)

E(eV) is the band gap of energy of the Porous Silicon (PS) substrate layers which can be measured by the photo luminesces of the peak in figure (3), which was (2.397 eV). The average pore diameter (d) for the Porous Silicon (PS) layer formed on the p-type Si (111) wafers was 4.83 nm and calculated using equation [14, 15]:

\[
E_{\text{gap}} = E_g + \frac{\hbar^2}{8a^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right)
\]

Where: \(E_g\) “the energy band gap of bulk c-Si“, “his Planck’s constant=4.13×10^{-15}\,\text{eV}\cdot\text{s}.”, whereas \((m_e^*)\), and \((m_h^*)\): the electron and hole effective masses, consecutively in \((300\,\text{K}, \ (m_e^*) = 0.19\,\text{mo},\ (m_h^*) = 0.16\,\text{mo},\) and \text{mo}: electron mass=9.109\times10^{-31}\,\text{kg}).

3.2. Surface Morphology
Figure 4 showed the TEM of Zinc Oxide (ZnO) image, the content of two types of nanoparticles spherical and few nanorods. Grain sizes of spherical particles limited between (6.5–23 nm). This results and TEM images of ZnO the thin film pattern agrees with [16, 17].
Figure 4. TEM image of undoped ZnO

Figure 5 illustrates SEM image of (n and p) type of the PS synthesize for 30 minutes with (30 mA/cm²) etching, so that the current density before and after deposit ZnO and ZnO: Al at 450°C, the grain size of thin films calculated by SEM shows in table (1). This behavior of grains arrangements is good agreement with reported [18, 19].

Figure 5. Scanning Electron Microscope images of up view of: a) p-type, b) ZnO/p-type, c) ZnO:Al 2%/p-type, d) ZnO:Al 4%/p-type, e) ZnO:Al 6%/p-type, f) ZnO:Al 8%/p-type.

Figure 6, measurement of Atomic Force Microscope shows the up view of the thin films, were the grain size be smallest with more adding more of, which was between the value of (62.2-25.6), the average of roughness be high quality when the aluminum increase as a doping in ZnO thin films which was between the amount (5.7-10.7nm).
Figure 6. 3D AFM image: a) p-type, b) ZnO/p-type, c) ZnO:Al 2%/p-type, d) ZnO:Al 4%/p-type, e) ZnO:Al 6%/p-type, f) ZnO:Al 8%/p-type.

AFM and SEM images of Zinc Oxide (ZnO) and ZnO with different concentration of Al thin films precipitate on the (n and p) types of PS shows that the grain size decreased and the roughness increased with the increase of aluminum ratio due to crystal distortion caused by the Aluminum concentrations, values of the grain size and roughness measured by AFM is shown in the table (1).

| Sample        | DSEM-PS (nm) | DAFM-PS (nm) | Sa (roughness average) (nm) |
|---------------|--------------|--------------|----------------------------|
| ZnO           | 48.3         | 62.2         | 5.7                        |
| ZnO: Al2%     | 37.5         | 47.4         | 7.4                        |
| ZnO: Al4%     | 29.4         | 41.7         | 8.6                        |
| ZnO: Al6%     | 27.1         | 33.5         | 9.2                        |
| ZnO: Al8%     | 21.3         | 25.6         | 10.7                       |

Table 1. Grain size calculated by AFM, SEM and roughness average of ZnO and thin films deposited on n-PS.

4. SENSING PROPERTIES OF CO GAS

The sensing mechanism of Zinc Oxide (ZnO) towards CO gas reliant on the reaction between the reducing gas and therefore the charged O$^-$ ions on the ZnO films surface, thereby inflicting a variation in the electrical phenomenon, as represented by equation [20]:

\[ \text{CO}_{(\text{gas})} + \text{O}^{(\text{ads})} \rightarrow \text{CO}_2 + e^- \ ... (2) \]

So that, by the electrons released back into the ZnO conduction band and increasing the carrier doped in the ZnO active layer, the resistance of the sensor is decreased upon exposure to a reducing gas [21]. Figure (7) shows the sensitivity is increased with the increase of aluminum concentration due to increases of aluminum electrons in the thin films so that the increase of aluminum-doped leads to improve the sensitivity.
Figure 7. Sensitivity for ZnO, ZnO: Al (2-8)% on p-type as a function of operating time for CO gas with concentration 1000 ppm at R.T.

Figure (8) the sensitivity of thin films deposited on the n-PS substrate is more than p-PS due to electrons carriers of an n-PS substrate. The carrier of aluminum is seen to increase with an increase in doping concentration. This caused the substituted implication of Al³⁺ ions at Zn²⁺ cations sites or the incorporation of the Al³⁺ ions in the interstitial positions [21-23].

Figure 8. Sensitivity for ZnO, ZnO: Al (2-8)% on n-type as a function of operating time for CO gas with concentration 1000 ppm at R.T.

Figures (9) show the sensitivity of films deposited on p-PS for the concentrations of 1000 ppm and substrate temperature, the sensitivity increases with increasing substrate temperature.

Figure 9. Change of sensitivity with temperature for undoped ZnO and ZnO: Al (2-8)% on p-type substrate for CO gas with 1000 ppm concentration.
ZnO and ZnO: Al thin films is higher sensitivity than using n-type substrate as shown in figure(10), the sensitivity increases with the temperature of the substrate arriving to 200°C then decreases with the temperature.

Figure 10. Change of sensitivity with temperature for undoped ZnO and ZnO:Al (2-8)% on n-type substrate for CO gas with 1000ppm concentration.

5. Conclusions
The average crystallite and grain size of the thin films of the pure ZnO and ZnO:Al were decreased with adding more quantity of aluminum. The average roughness of pure ZnO and ZnO: Al has been rise up with increasing a lot of Al with in the films as a doping, so that the thin films sensitivity increases due to increasing of the surface interactions of the thin films. For n-PS substrates, the sensitivity of the films was more than p-PS due to the increase of electrons in n-PS. Increasing substrate temperature leads to an increase in the sensitivity of the films, with optimum value for CO gas at 200°C for n-PS.

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