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Fabrication of ZnO Nanostructures Doped with Nb at Different Concentration as a Argon Sensor

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ABSTRACT

This works presents the report on the study of ZnO nanoparticles doped on silicon substrate. ZnO nanoparticles doped was prepared by using thermal immersion method with varies percentage ratio mass of dopant, Niobium. ZnO nanoparticles was characterized for their morphology by using field emission scanning electron microscopy (FESEM), crystalline graphic of material by x-ray diffraction (XRD) and electrical properties by IV measurement. The FESEM results showed that the randomly rougher distribution of ZnO nanoparticles doped with Nb covering on Si surface. XRD results reveals that ZnO nanoparticles doped with Nb was successfully growth on the silicon substrate. IV measurement was measured by 2-point probes. The measurement of the IV was done before and after sample exposed into argon gas. The argon gas was exposed for 10 minutes to indicate the sensitivity of the sample. The result shows that the sample that doped with 10wt% of niobium was the best sample to indicate the performance of the sensor compare to the other sample as observed in the 88.40% response when exposed to Argon gas.

1. Introduction

At the present time, there is an increasing demand for the progress of nano sized semiconductors due to their significant optical and electrical properties which are extremely useful for the fabrication of multifunctional nanoscale electronic and optoelectronic devices [1,2]. Nanomaterials are exceptional because of their optical, mechanical, catalytic, electrical, and magnetic properties [3-5]. Above and beyond, these materials also possess high surface area per unit mass. The specific surface area as well as surface to volume ratio increase drastically when the size of the material decreases. The size and geometry of the materials will have affected the movement of electrons and holes in the semiconductor. Ability of noble metal doping, high crystalline structure and competitive

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production rate upsurge the demand of fabrication nanoparticles for gas sensors application [6]. Semiconductor nanostructures have interesting physical, chemical properties and useful functionalities compared with their conventional bulk and molecular materials [7]. Nanoparticles have been recommended for numerous potential applications in electronics where quantum confinement affects in nanostructured semiconductors results in widening the band gap of semiconductor and acts as efficient light emitter. Nano-sized ZnO has attracted the interest of many researches because it shows better sensing properties than the bulk materials. Due to their size dependent properties, ZnO nanostructures are being widely used for gas sensing.

ZnO is a wide bandgap (Eg = 3.37 eV at room temperature) semiconductor material that has good sensing capacity. It is an n-type semiconductor material with hexagonal wurtzite and cubic zincblende structure [8]. Hexagonal form has the most stable structure at room temperature conditions compare to zincblande structure [9]. ZnO has various benefits such as low cost, abundant, non-toxicity, simplicity of fabrication, and easy to synthesis into various nanostructures materials such as nanoparticles, nanotubes, nanorods, nanowires, dandelion-like spheres, and nanowalls [10,11]. Nano-sized ZnO has been attracted interest from many researchers because of it showed better sensing properties than bulk materials. However, ZnO itself still has many deficiencies in term gas sensor application such as low electrical conductivity, poor selectivity, high working temperatures, and poor thermal. Yet, application of ZnO as a gas sensor still has many deficiencies such as a high working temperature, low electrical conductivity, poor thermal stability, reliability, and selectivity. A better performance of gas sensor can be improved by doped ZnO with doping materials. There are many types of dopant material that cn be used such as silver (Ag), gallium (Ga), iron (Fe), platinum (Pt) and aluminium (Al). ZnO nanostructure doped has a better conductivity, good carrier charge, easy to achieve and control [12], better stability and high transparency. Zinc Oxide is very suitable for transducer usage and sensor because of its relatively bio-safe and biocompatible material [13,14]. In recent times, the adjustment plan of doping ZnO with different materials such as semi-metals, noble metals, metal oxides and transition metals has been discovered as a useful approach to boost the ZnO gas sensing properties [15]. The application of niobium (Nb) doped with zinc oxide (ZnO) nanoparticles has not been discover yet. Nb is a paramagnetic metal belonging to group 5 in the periodic table with atomic number 41 (Z = 41) that has a body-centred cubic crystal structure [16,17]. The objective of this study is to produce high response of ZnO nanoparticles to the Ag gas. For that reason, Niobium is use as the dopant that can boost the performance and gas-sensing properties [18]. Lastly, to observe the performance of gas-sensing and structure properties when ZnO doped with Nb.

In this study, mainly attention is highlighting on the study of structural and electrical properties of zinc particles doped with niobium as a gas sensor. Thus, this study is to find the effect of doping material. The mass of the dopant is varied to study about their structural, electrical properties and their gas sensor performance. Solution-based synthetization such as thermal immersion method will be selected in this study since it is very simple, low cost and easy to be handled. The structural and electrical properties are characterized by using field emission scanning electron microscope (FESEM), x-ray diffraction (XRD) and IV measurement. Other than that, this research using niobium as the dopant with different mass percentage by using immersion method can be presented as references for other researchers to further study on this dopant type.

2. Methodology

Firstly, the Si wafer was cut into 2cm x 2cm pieces before cleaning process started. Then the silicon wafer was cleaned using acetone, methanol and diluted hydrofluoric acid (HF40%) with ratio 1:10 (HF40%:DI water) at 40°C for 5 minutes. Final step in cleaning process is dried using oven at 100°C for 3 minutes.

In order to prepare ZnO precursor, zinc acetate dehydrates, DEA and isopropyl are selected as starting material, stabilizer and solvent respectively in precursor preparation. First, zinc acetate dehydrates was dissolved in isopropyl. Then, DEA was added into the solution slowly to stabilize the reactions within the solution. After that, the solution was stirred and heated for 60 minutes at temperature of 60°C to yield a clear and homogenous solution. The solution continued stirred at room temperature for 24 hours [19].

Prepared ammonium niobate (v) oxalate hydrate to HMTA in 100mL volumetric flask varied with different mass ratio (5%, 10%, 15%, 20% and 25%) with zinc oxide nanoparticles solution. The solution was stirred and heated at 60°C for 1 hour. Afterward, the silicon substrate inserted into the test tube with 50mL solution with different mass ratio then immersed in water bath for 4 hours at 90°C. Later, the sample were dried in oven at 100°C for 10 minutes and annealed at 500°C for 1 hour.

All the sample was characterized by FESEM for morphology and elemental information magnifications at 10KX to 30KX. FESEM was used to confirm the present of ZnO nanoparticles doped with Nb on silicon substrate. Secondly, XRD is widely used for determine crystalline structure in a material. Then, the current-voltage measurement system comprises of a Keithly Source Meter (model 6430), with a convenient DMM interface and with I-V measurement capability ranging from 1100V to 10nV and 10.5A to 1fA.

Lastly, the sample was tested by using two-point probe to determine whether the sample doing well or not. The set-up of gas sensing was shown in Figure 1. The gas that used to measure the sensitivity of sample was Argon (Ar) gas and it exposed to gas for 10 minutes. After that, the IV characterization was measured. An electrical property is defined as the measurement of current-voltage of films before and after it exposed to the gas response of the gas sensor was determined by the gradient of the graph with formula in Eq. (1)

$$\text{Response (\%)} = ((R_o - R_s)/R_o) \times 100\% \quad (1)$$

where R_o is resistance before exposure, R_s is resistance after exposure.

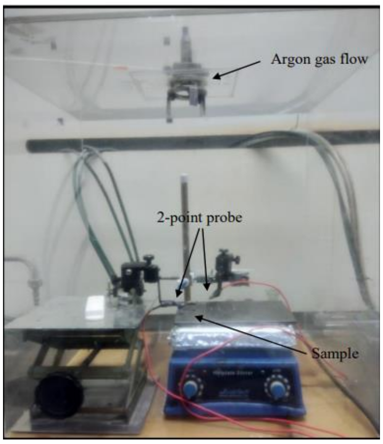

Fig. 1. Experimental set-up for gas testing

3. Results

3.1 FESEM Results

FESEM was used to investigate the morphology of the ZnO nanoparticles on Si substrates. Figure 2 shows the morphology of ZnO nanoparticles deposited on Si substrate with different mass ratio of dopant by thermal immersion method and undoped respectively. These images were show that ZnO particles undoped and doped were successfully synthesized on silicon substrate. The surface morphologies of ZnO nanoparticles doped with Nb reveal the randomly rougher distribution nanoparticles covering on Si surface as shown in Figure 2(a) to Figure 2(e). The FESEM results showed that their sizes were between 100~200nm. As the ratio mass percentage getting higher, the amount of ZnO nanoparticles that form on the silicon substrate getting lower as shown in Figure 2(a) to Figure 2(e). While, the FESEM images of undoped ZnO with magnifications of 30,000 exhibited the wire-like structures with diameter in the range of 100 nm showed in Figure 2(f).

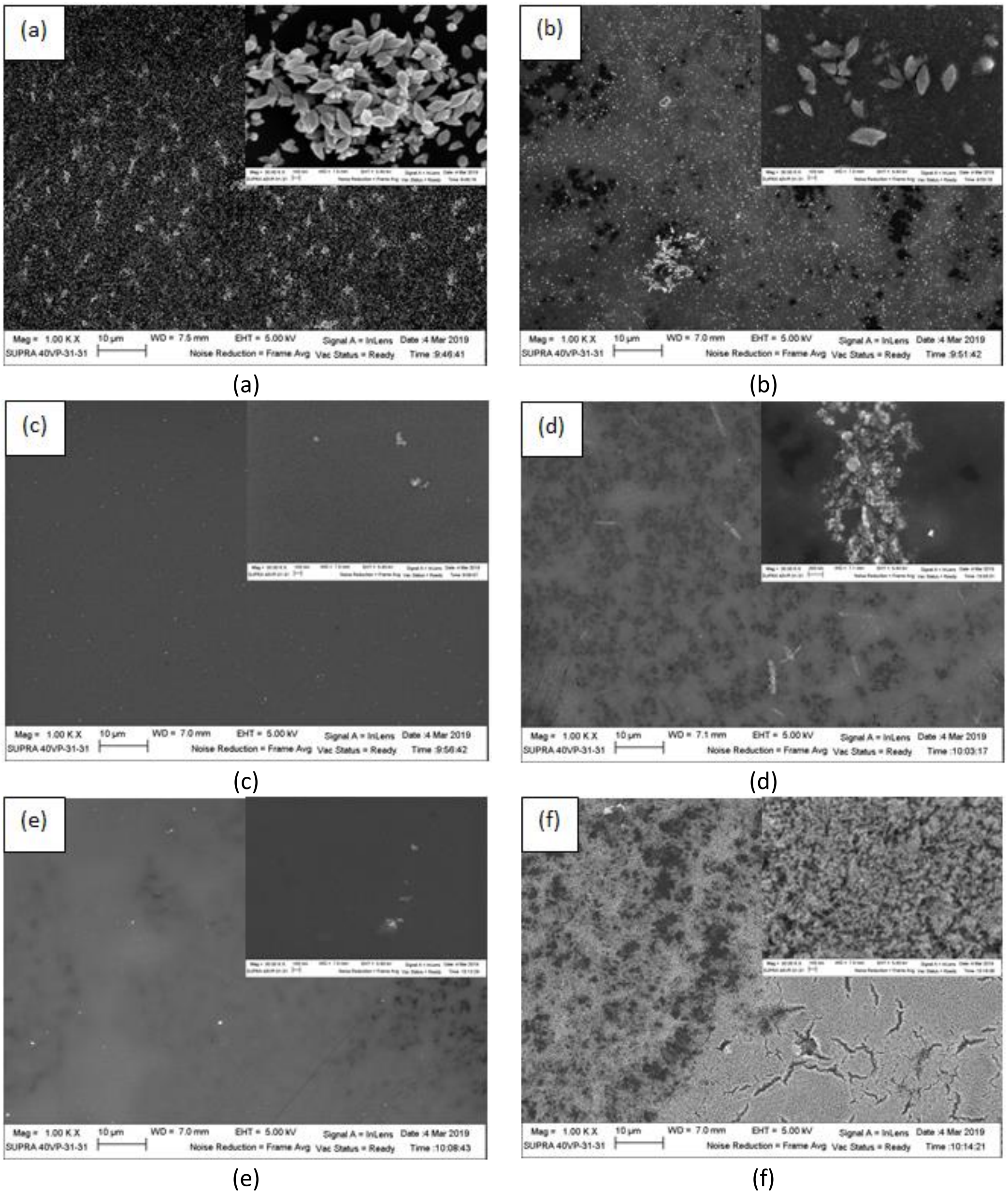

Fig. 2. FESEM image of ZnO nanostructure doped with Niobium with different mass percentage (a) 5wt% (b) 10wt% (c) 15wt% (d) 20wt% (e) 25wt% and (e) undoped ZnO

3.2 X-Ray Diffraction Results

Figure 3 shows the XRD spectra obtained from the ZnO nanoparticle on the Si substrate. It was observed that the latter dominants peaks were at 2θ = 33.057°, 33.34°, 33.27°, 33.33° and 33.095° which corresponding to ZnO undoped and ZnO with different mass percentage of dopant [20]. The peak of ZnO (100) is observed for the entire sample except in Figure 3(c), ZnO doped with 15wt% Niobium. The intensity of diffraction peak due to substrate phase is almost seems to have disappeared at Figure 3(c) to Figure 3(f) because of low content in term of Nb particles. It is observed that ZnO doped with 10wt% of Nb has the highest peak as shown in Figure 3. The crystallinity of ZnO particles increased for Figure 3(a), Figure 3(b), Figure 3(d), Figure 3(e) and Figure 3(f) because the peaks become sharper. As the ratio of mass percentage increasing, the crystallinity in the sample increased. For sample Figure 3(c), the crystallinity reduces probably because there is only some ZnO attached on the substrate. Addition of Nb dopants leaks to peak broadening, decrease in intensity of the peaks and slight shift to lower diffraction angles.

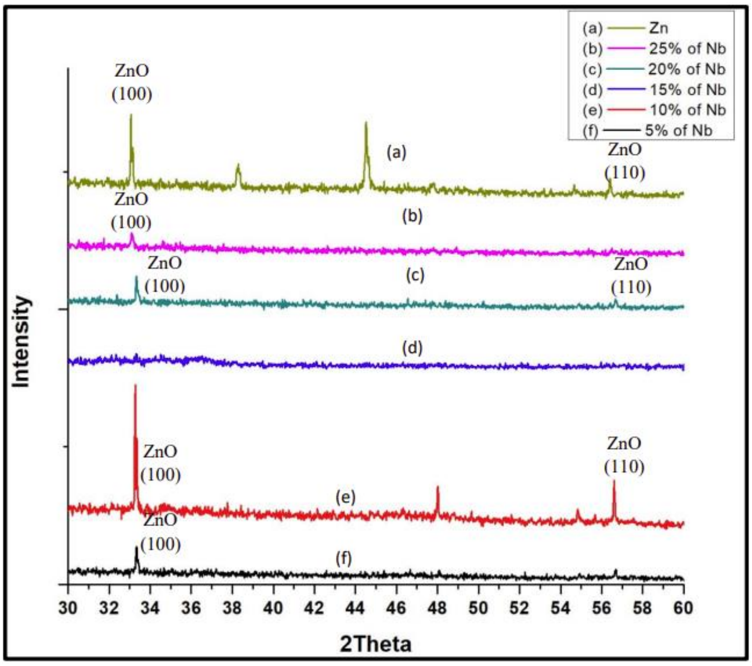

Fig. 3. X-ray diffraction pattern of the ZnO particle on thin film with different ratio mass percentage of dopant at range 2θ between 30° - 60°

By applying the Scherrer equation, the crystallite size was calculated [21]. As the ratio mass percentage of dopant increased, crystallite size decreased. For the mass percentage 5wt%, 10wt%, 20wt% and 25wt% of dopant, the crystallite sizes are 175.863nm, 365.432nm, 208.92 nm and 414.72 nm respectively. Table 1 below shows the crystallite sizes for ZnO (100) in different samples.

Table 1
The crystallite size for ZnO (100) in the different samples

Sample	Peak position (2θ)	FWHM (2θ)	Crytallite (nm)	Plane
(a) ZnO	33.087	0.0566	175.863	(100)
(b) ZnO doped with 25wt % Nb	33.095	0.038	414.72	(100)
(c) ZnO doped with 20wt% Nb	33.33	0.076	208.92	(100)
(d) ZnO doped with 10wt% Nb	33.27	0.080	365.432	(100)
(e) ZnO doped with 5wt% Nb	33.34	0.0906	175.863	(100)

Figure 4 showed the response of ZnO nanoparticles deposited on Si substrate with different ratio of mass percentage of dopant by I-V measurement (two-point probe) under air ambient. I-V measurement was used to obtain the current-voltage or resistance by providing a voltage-current stimulus and measure their reaction. Figure 4 showed the relationship of response and time at different samples of ZnO nanparticles; ZnO undoped, ZnO doped with 5wt%, 10wt%, 15wt%, 20wt% and 25wt% of Nb respectively. From Figure 4 it can be clearly seen that the response time increases with the presence of niobium. The sample prepared at 10wt% Nb showed higher sensitivity than the other samples, as observed in the 88.40% response when exposed to Argon gas. When the ZnO surface is exposed to argon, the reaction between the solution and the oxygen species adsorbed on ZnO surface causes a change in resistance value. The methanol molecules release the electrons and decrease the number of surface-adsorbed oxygen species. Therefore, the thickness of the depletion region increases and the resistance decreases. ZnO nanoparticles doped with 15wt%, 20wt% and 25wt% of Nb (d, e and f) does not give best response when exposed to argon gas because the amount of ZnO nanoparticle form very small and almost not seen from the FESEM and XRD method.

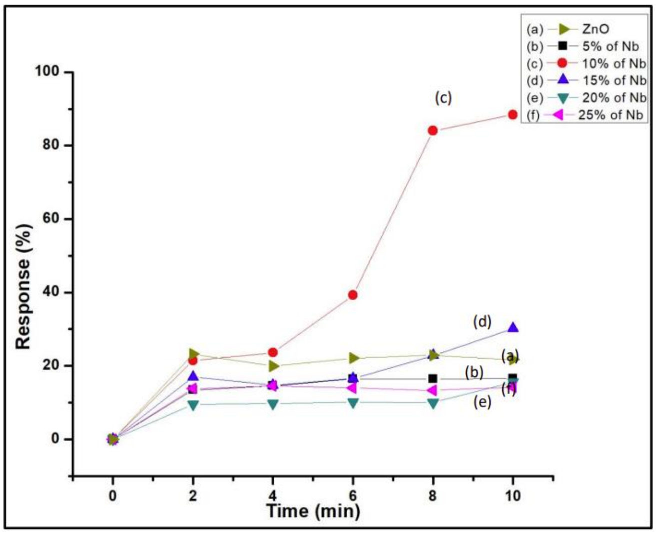

Fig. 4. The responses of the ZnO nanoparticles doped Nb exposed to the Argon gas in 10 minutes at room temperature

4. Conclusions

Results were shown that there are different structures and image can be producing by ZnO nanoparticles with different ratio mass percentage of dopant that deposited on Si substrates. Normalized the sensitivity of ZnO doped with niobium very fast response-recovery due to gas sensor. The effect of different ratio mass percentage of dopant on the sensitivity of sensor was investigated. It was found that sensor with 10wt% of dopant on ZnO nanostructure show better response than other mass percentage. As the ratio of mass percentage of dopant increased, the amount of dopant that attached on the zinc oxide nanostructures become reduces. Thus, 10wt% of dopant on silicon substrate is seemed to provide the better structure and good resistivity.

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