Temperature Effect of Chemical Bath Deposition (CBD) to Fabrication and Characterization of Zinc Oxide Nanorods Thin Films Based Gas Sensing: Ethanol

Adimas Ramadhan[1], Ni Luh Wulan Septiani[2], Wahyu Aji Eko Prabowo[3,4], Asih Melati[1,*]

[1]Department of Physics, Faculty of Science and Technology, Universitas Islam Negeri Sunan Kalijaga, Yogyakarta 55281, Indonesia
[2]Advanced Functional Materials Laboratory, Engineering Physics Department, Faculty of Industrial Technology, Institut Teknologi Bandung, Bandung 40116, Indonesia
[3]Research Center for Quantum Engineering Design, Faculty of Science and Technology, Universitas Airlangga, Surabaya 60115, Indonesia
[4]Informatics Engineering Department, Faculty of Computer Science, Universitas Dian Nuswantoro, Semarang 50131, Indonesia

E-mail: asih.melati@gmail.com

Abstract. Fabrication of zinc oxide (ZnO) nanorods thin films based gas sensing ethanol have been done. Ethanol belongs to volatile organic compound (VOC) that are dangerous if inhaled by humans in high concentrations, so that its detection is necessary. Temperature as kinetic controller of chemical bath deposition (CBD) process take effect to ZnO fabrication and characterization. ZnO nanorods thin films was synthesized onto glass substrate by dip-coating technique. ZnO nanorods was grown using $Zn(NO_3)_2.4H_2O$ and HMTA with ratio 1:1 under CBD condition at temperature 75ºC, 83ºC, and 87ºC. Result of SEM showing ZnO CBD 83ºC has nanorods shape with diameter size is 95.56 nm, furthermore at 75ºC the formation of the nanorods was not completed yet while at nanorods became deconstructed. XRD result showed all of ZnO sample have hexagonal wurzite which are match well with ICDS-094004 card. Ethanol gas sensing tested at 100ºC, 150ºC, 200ºC showed high sensitivity of the sensor up to 77.31% for ZnO CBD 75ºC at 100ºC. ZnO CDB 83ºC sample at test 200ºC have highest response on 2.22 min (t_{res}) and 0.45 min (t_{rec}). Time respond and recovery will increase along with increasing of test temperature.

Keywords: Chemical bath deposition, ethanol, gas sensing, temperature effect, ZnO nanorods thin films

1. Introduction

Recently, air pollution is becoming worse so that it needs more concern. Air pollution can be happened indoor or outdoor. Outdoor pollution is emitted by vehicle exhaust, industry, wood burning, and volcano activity. Indoor pollution is emitted by paint, perfume, chemical reagent or building property. Indoor pollution is more dangerous to health than outdoor pollution as all human activities are mostly in the room. Generally, indoor pollution belongs to volatile organic compounds (VOCs) [1, 2]. OSHA reported that ethanol is a part of VOC.

Ethanol is colourless, volatile and flammable substance. This substance generally used as the main chemical reagent in chemical industry, solvent of paints, used as cleaner in medical use [2, 6]. Inhaling ethanol in high concentrations can result in health problem such as headaches, eyes of irritation,

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nausea, mucous membranes in system of respitory, drowsiness, and general malaise [10]. Hence, monitoring the pollution concentration is very important and the primary instrument monitoring is a gas sensor.

Compared to other kinds of sensors, gas sensor based on metal oxide semiconductor are most promising [11] to develop since it has high sensitivity and chemical stability [4]. Metal oxide semiconductors such as SnO_2, ZnO, WO_2, TiO_2 and TiO_2 are normally used as gas sensor [1, 3]. Zinc oxide (ZnO) is an n-type direct wide band gap (E_g = 3.35 eV) and most popular gas sensor since it has several advantages namely; low synthesis temperature, high sensitivity, good stability and morphology controllable [3, 13, 14].

Morphology is one of important parameter in gas sensor which determine sensitivity because it relate to specific surface area directly. Until now, there are many shapes of ZnO include to nanowires, nanobows, nanocages [5, 7], nanorods, nanobelts, nanosheets [3, 8, 9]. ZnO has high resistance with range resistivity 10^{-3}-10^{5} Ωcm at room temperature, while as gas sensor, ZnO operation temperature is relatively high and lead to high power consumption [12].

Nowadays, the important parameter is to get high sensitivity of ZnO at low temperature and decrease of the size. Septiani *et al* [4] reported that ZnO nanorods belongs to one-dimensional (1D) nanostructure and has a high density meanings to relatively high sensitivity. Therefore, the more nanorods size decreases, the more surface area increases and lead to a high density then effect to high sensitivity of ZnO. However, ZnO thin film form have been reported more sensitive than the others form like single crystal, thick film, and hetero-junctions [10].

In this research synthesis of ZnO nanorods was conducted by chemical bath deposition method with various of temperature. Seed layer of thin film on glass substrate was grown by dip-coating technique. The result of ZnO nanorods thin films were characterized by scanning electron microscopy (SEM) and x-ray diffraction (XRD) in order to investigation the surface structure. And then, the result have been tested to ethanol gas sensing. The different of temperatures operation on chemical bath deposition have been studied and the result indicate not only the effect to fabrication and characterization of the samples, but also the effect to sensor performance too.

2. Method

Synthesis of ZnO thin film was initiated by seed layer deposition on glass substrate by dip-coating technique. Typically, 2.6 g $ZnO(NO_3)_24H_2O$ was dissolved in ethylene glycol 60 ml and 0.160 g diethanolamine to get homogeneous solution under vigorous stirring at 70ºC. The glass substrates were dipped into the solution four times with speed control 3V and then calcined at 350ºC for an hour.

Nanorods were grown by CBD method. 1.97 g $ZnO(NO_3)_24H_2O$ and 1.26 g hexamethyle tetra amine (HMTA) was dissolved into ethanol 15 ml and aquabides 45 ml solution and stirred for 90 minutes. The resulting substrates of dip-coating process were immersed vertically into the reaction bath in CBD chamber. The detail chemical reactions involved on CBD process are given as follows:

$$Zn(NO_3)_2.4H_2O \rightarrow Zn^{2+} + 2NO_3^- \quad (1)$$
$$(CH_2)_6N_4 + 6H_2O \leftrightarrow 6HCHO + 4NH_3 \quad (2)$$
$$NH_3 + H_2O \leftrightarrow NH_4^- + OH^- \quad (3)$$
$$2OH^- + Zn^{2+} \leftrightarrow Zn(OH)_2 \quad (4)$$
$$Zn(OH)_2 + Zn(OH)_2 \rightarrow 2Zn\text{-}O\text{-}Zn + 2H_2O \quad (5)$$
$$2Zn\text{-}O\text{-}Zn + O_2 \rightarrow 4ZnO_{(s)} \quad (6)$$

The functional of HTMA to made rods growth cause of its cyclic structure. Temperature operation of CBD chamber was variated at 75ºC, 83ºC, and 87ºC each of all for 3 hours. After deposition the substrates were rinsed with aquabides, dried and then calcined at 350ºC for a hour.

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The crystal structure of resulting ZnO nanorods thin films was determined by X-Ray diffraction (XRD) using a Philips 1835 diffractrometer scanning with Cu Kα radiation (λ = 1.54060 Å) generated at 40 kV. The machine was set to scan mode for 2θ interval of 10-90°. Then the surface morphology of ZnO nanorods thin films were observed by scanning electron microscopy (SEM) using Jeol JSM-6510LV (Japan) low vacuum.

ZnO nanorods thin film within silver paste dropped into resulting substrates using doctor blade which after deposition processing was calcined at 300°C for a hour. The illustrasted of silver paste deposition on substrates shown in Figure 1.

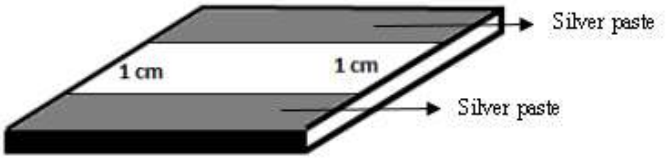

Figure 1. Illustration of silver paste deposition on substrates

The sensor performance was tasted using gas sensor characterizations which shows in Figure 2. Nitrogen used as gas carrier for ethanol gas and the concentration of ethanol 200 ppm was fixed and the tests were performed at 100°C, 150°C, and 200°C. Firstly, ethanol and nitrogen were mixed before introduced to the chamber testing, and the air exposed to the sample inside the sensors chamber. The sample was connected with Picotest M3500A as data logger and the resistance changing of the gas sensor sample, while before and after exposure of ethanol gas was measured by the instrument.

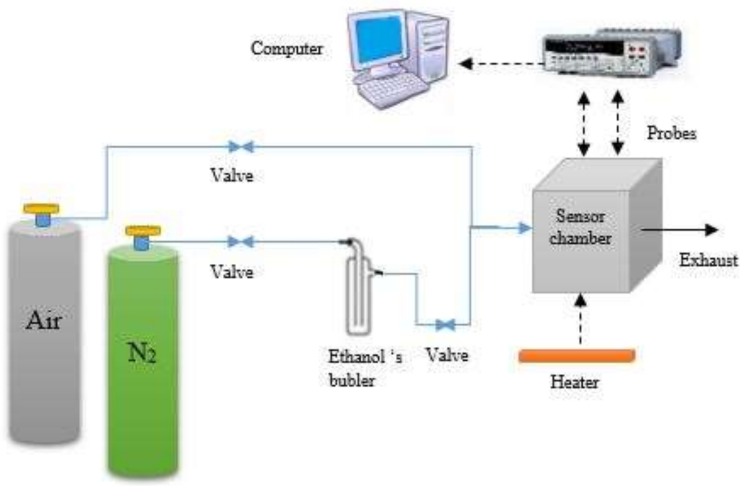

Figure 2. Illustration of ethanol gas sensing characterization system

3. Results and Discussion

Figure 3 shows the X-ray diffraction patterns of ZnO nanorods thin film. High peaks indicated all samples have good crystallinity. Furthermore, all of ZnO samples have a hexagonal wurzite crystal structure, which confirmed by ICDS-094004. The diffraction planes are (100), (002), (101), (102), (110), (103) and (112). The good crystallinity of ZnO nanorods thin films is predicted to have a good potential in applying as a gas sensor. Diffraction angles at ZnO samples can be seen in Table 1.

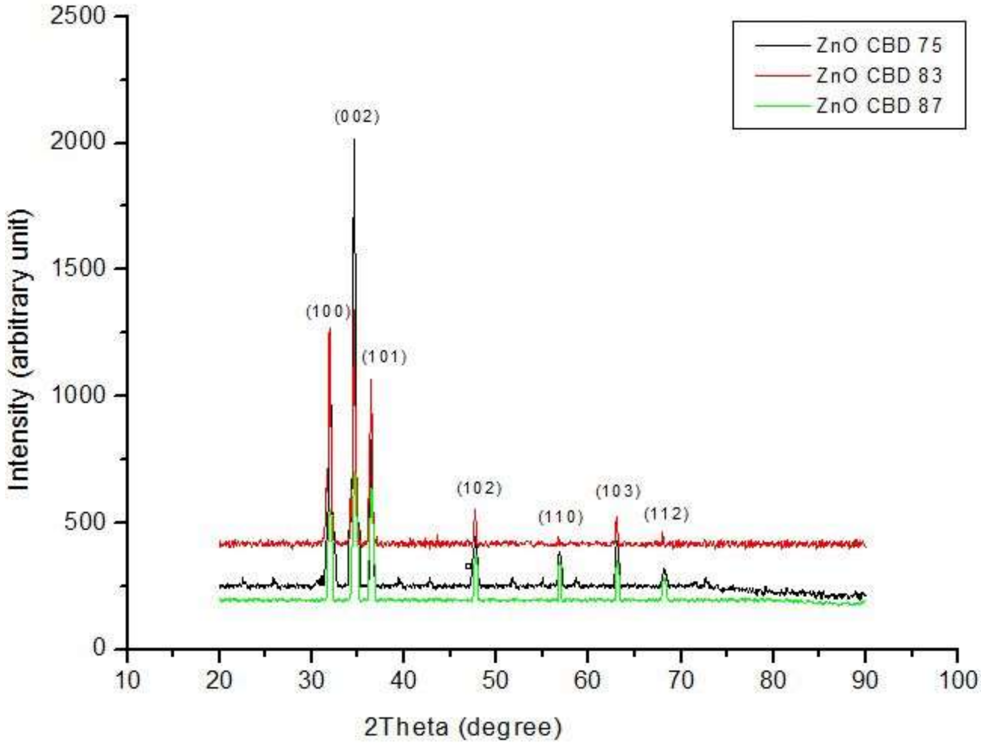

Figure. 3 X-ray diffraction patterns of ZnO nanorods thin films samples

Table 1.Diffraction angles at various of ZnO

ZnO	2θ (º)						
ICDS-094004	31.80	34.45	36.29	47.58	56.66	62.91	68.02
CBD 75	31.98	34.56	36.44	47.72	56.84	62.20	68.14
CBD 83	31.90	34.56	36.38	47.72	56.70	62.98	68.02
CBD 87	31.98	34.62	36.44	47.72	56.80	63.06	68.14

Figure 4a, 4b and 4c show the result of the morphology of ZnO nanorods thin films. From SEM analysis, the different in temperature cause the result of different ZnO shapes. All samples shows hexagonal shapes nanorods. For the sample ZnO with CBD 73ºC, the shapes grow on sheets and rods form, where rods raise up between of sheets. This phenomena cause of grain effect as seed layer not optimize to growing rods. This condition explain the shapes of sheets turned into rods. The rods in this sample has a diameter around 240.33 nm.

For ZnO sample with CBD 83ºC show a rods shape with the hexagonal structure that optionally spread evenly over the substrate with the diameter of rods around 95.56 nm. Meanwhile the ZnO sample with CBD 87ºC show a surface rods shape predominantly with little sheets. In this sample, rods were reconstructed into sheets with the diameter of the rods around 344.11 nm.

In CBD process, there is a reduction in energy activity towards the growth of ZnO so it gives an uneven effect on the shape of rods which can cause sheets or deconstruction of rods to become sheets. The temperature and operating time in the CBD process are important parameters which provide an effect during the growth of grain into rods. Under the same conditions, the higher the temperature is proportional to the higher the nanorods that grow.

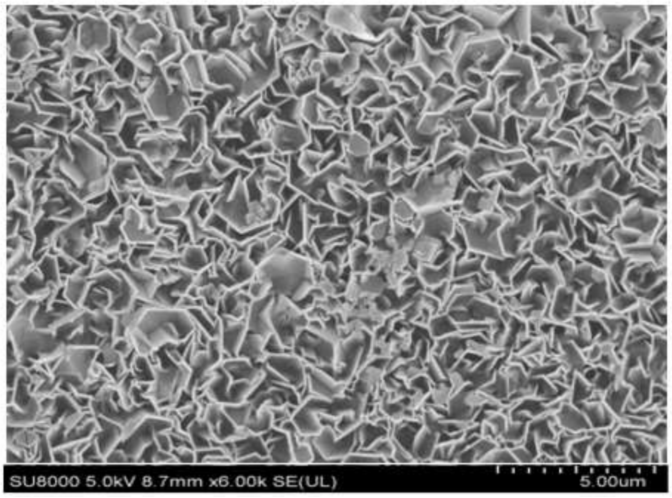

Figure 4a Scanning electron microscopy (SEM) image of ZnO CBD 75

Figure 4b Scanning electron microscpy (SEM) image of ZnO CBD 83

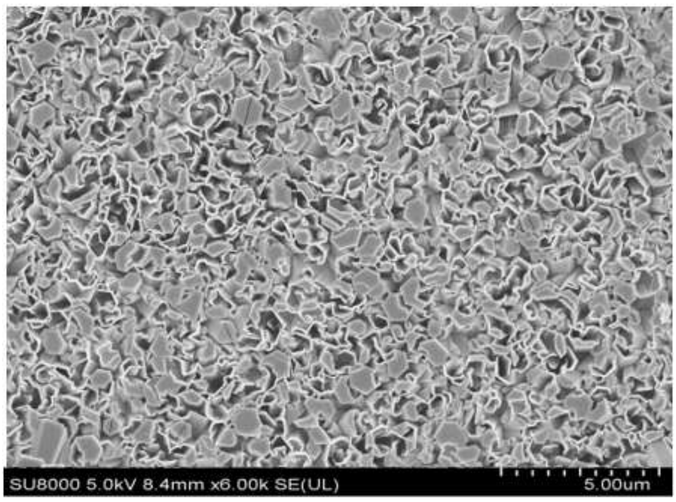

Figure 4c Scanning electron microscopy image of ZnO CBD 87

Figure 5-7 show ZnO nanorods gas sensor resistance record data on ethanol gas exposure shows a significant difference. For samples ZnO CBD 75 with temperature operation on sensor chamber at 100ºC, the resistance record is stable so that ethanol gas can be exposured and obtain data to determine the sensitivity of sensor. When the temperature operation is at 150ºC and 200ºC, the resistance record shown unstable then exposure still unstable. ethanol gas, while even not stability conditions where not to known sensitivity of sensor. In the ZnO CBD 83 sample the resistance is stable so that data can be obtained to determine the sensor response. N/A occurs in the resistance of ZnO CBD 87 so that the sensor response cannot be known.

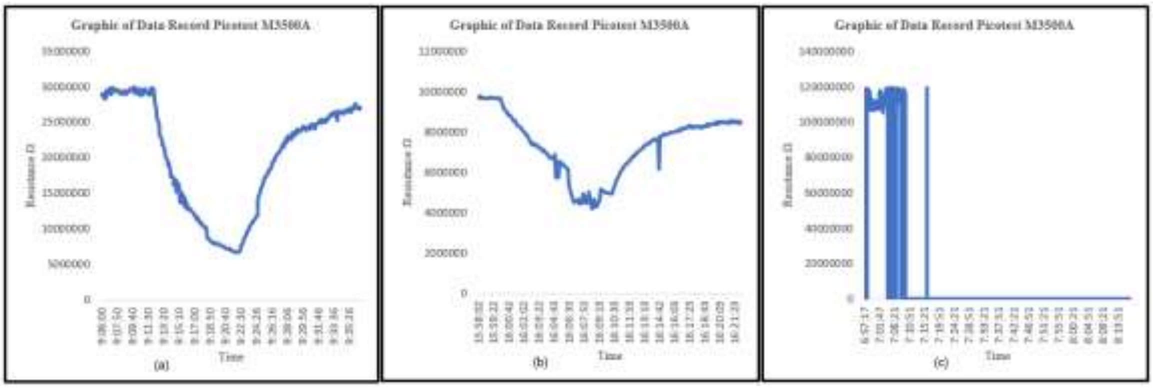

Figure 5. Graphics of data record picotest M3500A on exposure of ethanol gas at 100ºC base on ZnO sample. (a) CBD 75, (b) CBD 83 and (c) CBD 87

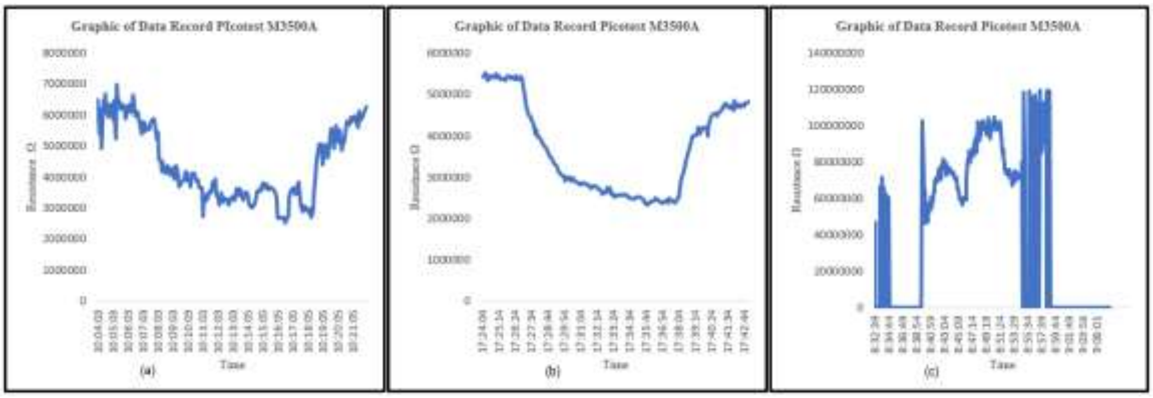

Figure 6. Graphic of data record picotest M3500A to exposure of ethanol gas at 150ºC base on ZnO sample. (a) CBD 75, (b) CBD 83, and (c) CBD 87

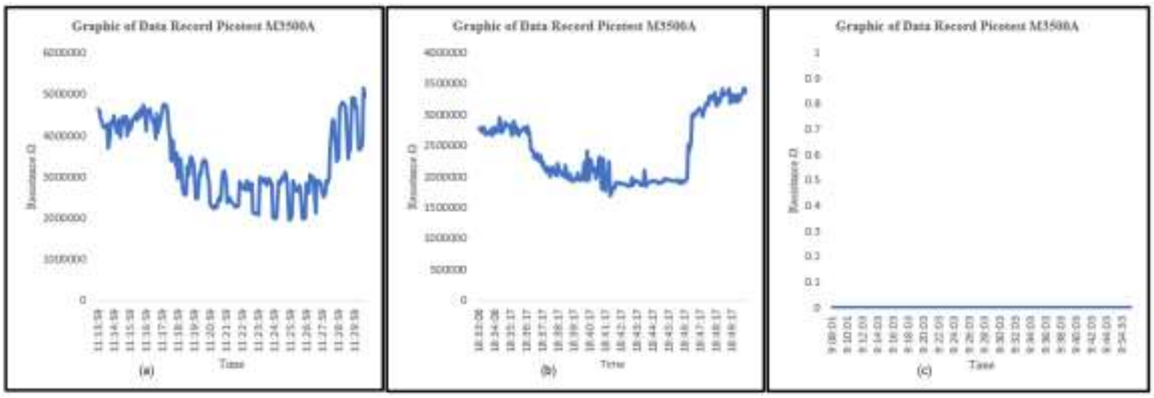

Figure 7. Graphic of data record picotes M3500A to exposure of ethanol gas at 200ºC bases on ZnO sample. (a) CBD 75, (b) CBD 83, and (c) CBD 87

ZnO is n-type semiconductor which has more hole that oxygen atom can give donor of electron. When ZnO was exposed free air, the oxygen will be adsorbed, dissociated, and obtain an electron from result from conductivity in depletion layer in surface. Oxygen change to different type of ion depend on temperature. At temperature under 150^{o}C, it changed to molecule ion of O_2^-, while at the temperature more than 150^{o}C, it will changed to ion of O^- . In the case of 400^{o}C, it dominated by O^{2-}. Molecule ion of O_2^- and atomic ion of O^{2-} are unstable hence it not influenced by gas sensor mechanism. Reaction of ion oxygen were given following this measurement:

$$O_2 + 2e^- \rightarrow 2O^- \quad (7)$$

Ethanol as gas target is an electron donor type, reducing gas when it interact with ZnO and will be produce CO_2 and H_2O. The electrons will back to conduction band lead to a decrease of resistance cause of depletion layer is narrowed down. Free air flow is flowing and ethanol expose is stop, the surface will refill again with oxygen ion that effect to depletion layer and lead to increase the resistance.

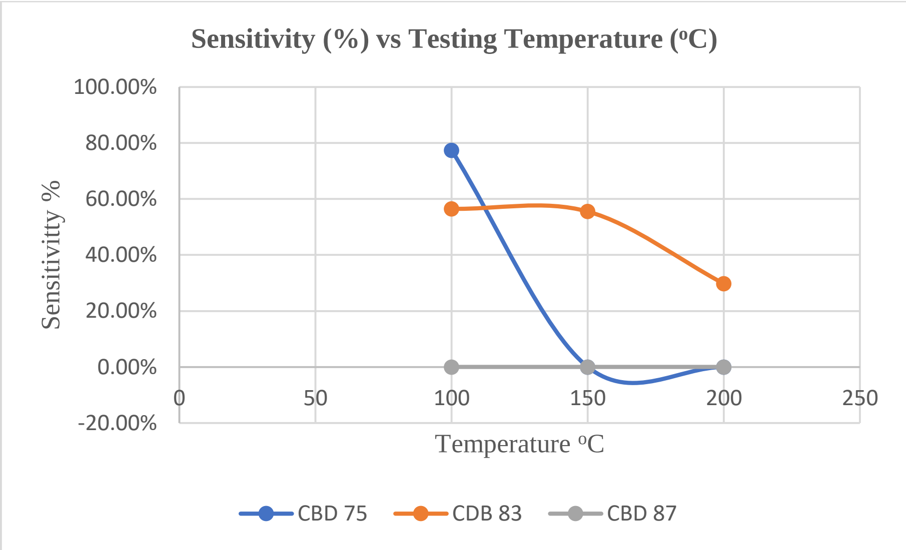

Figure 8. Graphic of sensitivity bases samples ZnO to various of testing temperature

The Figure. 8 shown the performance sensitivity of sensors based ZnO nanorods thin films. The sensitivity of sensor measurement was given this equation:

$$\text{Sensitivity (\%)} = \left(\frac{\text{Ra}-\text{Rg}}{\text{Ra}}\right) x\ 100\% \quad (8)$$

The sensitivity increase depend on certain temperature which mean the optimal temperature show the maximum performance. Those condition obtained by surface material sensor of oxygen ions on maximum while total of gas interaction was maximum. This was shown to sample ZnO CBD 83, the optimum point at 100^{o}C on 56.50 % sensitivity and then decrease at 150^{o}C and 200^{o}C around 55.51 % and 29.74 %, respectively.

Table 2 indicate the dynamic characterize of sensor which mean that time response and recovery equal with the sensitivity of sensor. Previous research has been reported that a high sensitivity increase with lead to a high time response and reocvery, while linear to increase of temperature operation and consentration exposure of gas target except to optimum point which can be see on data time response and recovery of sample ZnO CBD 83.

Table. 2 Dynamic characteristics of sensor bases ZnO nanorods thin films to ethanol gas

T (°C)	CBD 75			CBD 83			CBD 87		
	S (%)	t_{Res} (min)	t_{Rec} (min)	S(%)	t_{Res} (min)	t_{Rec} (min)	S(%)	t_{Res} (min)	t_{Rec} (min)
100	77,31	6,25	4,58	56,50	7,28	6,26	-	N/A	N/A
150	-	-	-	55,51	5,3	2,56	-	N/A	N/A
200	-	-	-	29,74	2,22	0,45	-	N/A	N/A

The highest sensitivity 77.13% was given by sample ZnO CBD 75 at 100°C of temperature operation sensing. The highest time response is 2.22 min and the recovery is 0.45 min were given by sample ZnO CBD 83. Those conditions relation with shape of structure ZnO nanorods thin films. Moreover, the morphology of material determined by oxygen ions when adsorption process ongoing.

Morphology structure of ZnO sample at CBD 83 was exhibited nanorods homogenous and spread evenly that effected has response stability. For sample ZnO sample at CBD 75 explain to construction process on nanorods which still steady state and responsible at 100°C of temperature operation. N/A occurs in the ZnO sample at CBD 87 which shows the deconstruction process of nanorods because of the weak effect of force bonding activity on the surface when gas exposure takes place, initially it can respond but there is no continuation of the gas and the target gas is missed.

4. Conclusion

Fabrication ZnO nanorods thin films have been done to create by chemical bath deposition method with precursor of $Zn(NO_3)_2 4H_2O$ and HTMA (1:1) at different temperature 75°C, 83°C, and 87°C. The different of temperature that effect to sample resulting to characterization such as the shape and morphology. The great sample get on ZnO CBD 83 with homogenous hexagonal wurzite structure which spread evenly with diameter size about 95.56 nm. This sample show on great responsible too of performance ethanol gas sensor sensitivity up to 56.50 % with time respond 7.28 min and recovery 6.26 min. ZnO CBD 75°C explain to nanorods constructed (sheets to rods) and ZnO CBD 87°C explain to nanorods deconstructed (rods to sheets). Time respond and recovery will increase along with increasing of test temperature except has been on optimum point. Test temperature at 100°C is the optimal which sensitivity up to 77.31 % (ZnO CBD 75°C) and 56.5% (ZnO CBD 83°C).

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