Effect of Substrate Temperature on the Electrical Properties of Nanostructured Zinc Oxide Thin Film for Ammonia Sensor Application

MUHAMMAD KHAIRI BIN ABDUL SATAR
2009802616
Faculty of Electrical Engineering,
Universiti Teknologi MARA Malaysia
Email: khairisatar@gmail.com

***Abstract*-This project focuses on the effect of substrate temperature on the electrical properties of nanostructured zinc oxide thin film for the ammonia sensor application. Nanostructured zinc oxide thin film has been deposited on the thermally oxidized SiO_2 using radio frequency (RF) magnetron sputtering at various temperatures range from room temperature to 500ºC. The thickness of the thin film was measured using surface profiler. The surface morphology and grain size were measured using field emission scanning electron microscopy (FESEM). The grain size were increased with the increased of substrate temperature. The effect of substrate temperature on the electrical properties and sensitivity has been investigated. The highest percentage of sensitivity is at room temperature that is 94.5%.**

Keyword-ammonia sensor, zinc oxide, RF magnetron sputtering

I. INTRODUCTION

Nowadays, the scientist and researcher around the world have given more attention on nanotechnology. Nanotechnology induced to science and technology with the possibilities to manipulating atoms and molecules at nanolevel [1]. The word nano that's mean 10^{-9} and it is hundred thousand smaller than human hair that is 100 micrometer [2].

Ammonia is widely used in industry therefore the monitoring of its leakage is crucial. Ammonia consists of one particle of nitrogen and three particle of hidrogen (NH_3). It is chemicals that produced by human and nature [10]. The major use of ammonia are fertilizer, animal feed production smelling salts, household cleaners, window cleaning products, explosives, paper, and rubber [11]. Ammonia gas is colorless at room temperature and has very sharp odor that make suffocating odor [10]. Ammonia is a corrosive substance and can cause permanent blindness, lung disease, or death if the ammonia directly contact in high amount or frequently. If accidently drank, it can burn in mouth, throat and stomach [10].

Ammonia sensor can be used in variety application such as in industry, medical, agriculture and environment monitoring [3]. A good ammonia sensor must have good characteristic such as high sensitivity, low resistance, time response, reliable and cost effective [3].

There are many metal oxides material that used for ammonia sensor such as tin oxide, zinc oxide and titanium oxide. Among all these material, zinc oxide has been chosen in this research because wide band gap, low cost, large exciton binding energy, stable wurtzite structure and its superior optoelectronic characteristics [2, 6, 13]. The wide and direct band gap of zinc oxide is 3.37 eV and large exciton binding energy of zinc oxide is 60 meV at room temperature [2, 3, 4 5, 6, 7]. The advantages of wide band gap are higher breakdown voltage, ability to sustain large electric field, lower electric noise, operate in high temperature and high power operation.

Due to the good properties of zinc oxide, there are various applications from zinc oxide such as room-temperature and high-temperature ultraviolet (UV) lasers, light emitting diode, surface acoustic wave devices and gas sensors [4, 5]. Zinc oxide is n-type and known as II-VI compound semiconductor and with the formula ZnO [2, 4, 5, 6]. It is a hardest because it's melting point which decomposes into zinc vapor and oxygen at 1975ºC or 2248K [2, 6]. Zinc Oxide has stable wurtzite structure with lattice spacing, a=0.325 nm and c=0.521 nm [2, 5, 6].

The properties of thin film are affected by several factors such as substrate temperature, annealing temperature, deposition time, type of substrate and RF power used. Although there are many factor affected the properties of the prepared ZnO but this project only focus on the effect of substrate temperature to the electrical properties and the sensitivity of the gas sensor. The substrate temperature variation is from room temperature to 500°C.

ZnO thin films have been prepared by various techniques, such as R.F. magnetron sputtering, reactive magnetron sputtering, chemical vapor deposition, ion-beam evaporation, electron-beam evaporation, spray pyrolysis, laser ablation and sol-gel process [12, 13]. Among the method, RF magnetron sputtering have advantages that are good adhesion of films on substrates, high deposition rate, and process parameter easy to control [6, 13].

The performance of gas sensor depends on the few factors such as expose surface area. Due to the size of zinc oxide nanostructures that provide large expose surface area to volume ratio to increase the sensitivity of the gas sensor [8, 9].

The objectives of the project are to deposit nanostructured zinc oxide via RF magnetron sputtering method and study the effect of substrate temperature on the morphology, electrical properties and sensitivity of zinc oxide thin film towards ammonia gas.

II. METHODOLOGY

Generally this project involves six steps which are substrate cleaning, growth of silicon oxide, deposition of zinc oxide thin film, annealing process, characterization that consist structural characterization, electrical characterization and sensitivity test. Figure 1 summarized the overall flow of this project.

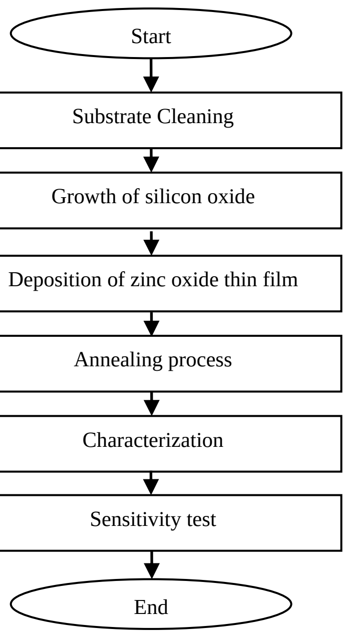

Figure 1: Project Flow Chart

Substrate Cleaning

In the substrates cleaning process, the 2cm X 2cm silicon substrates were cleaned using acetone, methanol and DI water by ultrasonic bath for 10 minutes. After cleaned by methanol, the substrates are cleaned by hidro fluoric (HF) for fifteen second. The ratio of hidro fluoric to the water is 1:10. For every cycle the sample was rinse with DI water. Finally the substrates were dried by nitrogen gases. These processes were done to ensure that all organic and inorganic contaminations were removed from the substrates.

Growth of silicon oxide

The next stages are the growth of silicon oxide (SiO_2) using high temperature furnace. The substrates will be exposed to the oxygen at elevated temperature in the furnace in specific time and temperature. The thermal oxidation of silicon substrates were done at 1000^{o}C for 60 minutes with 1L/m of oxygen flow rate. Figure 2 summarized the heating profile of thermally grown SiO_2.

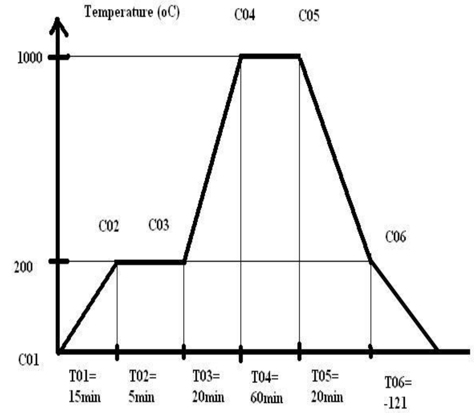

Figure 2: grown silicon oxide (SiO2) stage

Deposition of zinc oxide thin film

Nanostructured zinc oxide thin film were grown on silicon substrate using RF magnetron sputtering with variation of substrate temperature that is room temperature, 100^{o}C, 200^{o}C, 300^{o}C, 400^{o}C and 500^{o}C and others sputtering parameter were maintain such as RF power are maintained at 50W and sputtering pressure are maintained at 8 mtorr. The sputtering system was pumped down to $5X10^{-5}$ torr. A high purity (99.99%) ZnO target of 2-in. diameter and 3 mm thickness was used for the sputtering. Sputtering gas that was used is argon gas and the flow rate of argon gas is 45 standard cubic centimeters per minutes (sccm). The 1 hour of deposition was carried out after 60 second of pre-sputter to remove any impurity on the surface of the target.

Annealing process

The annealing process was carried out using high temperature furnace at 500 °C under oxygen ambient.

Characterization

1. Structural Characterization

Surface Profiler

The thickness of zinc oxide thin film was measured using Veeco Dektak 150 Stylus Surface Profiler. The deposition rate is the rate of deposition on the substrates during sputtering. The deposition can be calculate by formula of deposition rate is shown in equation 1.

D.P = T/t ………………….. (1)

Where

D.P=deposition rate

T=thickness of zinc oxide thin film

t=deposition time

FESEM

The surface morphology of the zinc oxide thin film was characterized using JEOL JSM-7600F, field emission scanning electron microscope.

2. Electrical Characterization

Aluminium metal contact has been deposited into substrates using thermal evaporation. The metal contact thickness is 60nm. The current voltage measurements were done using ADCMT 6243 voltage current source/ monitor. The voltage varies from -10 to 10V. After the current has been measured, the resistance can be calculated using equation 2.

V=IR……………… (2)

R=V/I

Where

V= voltage

I=current

R= resistance

The resistivity was calculated using the equation 3.

p=(R x T x W)/L…………….. (3)

Where

T= film thickness

W= length of metal contact

L= length between metal contact

The conductivity was measured using equation 4.

σ= 1/p……………… (4)

Where

σ= conductivity

p= resistivity

Sensitivity Test

Figure 3 show the configuration of ZnO based ammonia sensor. During this measurement, the current has been measured.

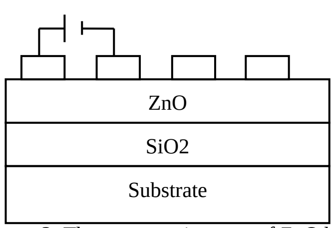

Figure 3: The cross section area of ZnO based NH_3 sensor

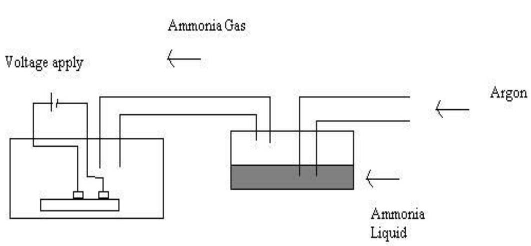

Figure 4: Sensitivity test set up diagram

The sensitivity of the ammonia (NH_3) sensor was measured using the ammonia sensor setup as shown in Fig. 4. The ammonia solution was heated at 50˚C to produce NH3 gaseous and the flow rate of carrier gas (Ar) is 300ml/min at 1 bar while the voltage was varied from -10 to 10 V. The sample box and the solution container were sealed to prevent any leakage. The measurement was done at room temperature. The formula to calculate sensitivity is shown in equation 5.

Sensitivity = $\frac{Rg-Ra}{Rg}$ **X 100**…………………….. (5)

Where

Ra=resistance of thin film at ambient environment

Rg= resistance of thin film under the test gas

III. RESULT AND DISCUSSION

1. Structural Properties

Surface Profiler and Deposition Rate

Varying Temperature (ºC)	Average Thin Film Thickness (nm)	Deposition Rate (nm/m)
R.T	84.9	1.415
100	103.1	1.718333
200	51.3	0.855
300	46.7	0.778333
400	48.0	0.8
500	44.1	0.735

Figure 5: Table of ZnO thin film thickness and deposition rate

Figure 5 show the data table of the thin film thickness and deposition rate. The zinc oxide thin film thickness is decrease with the increasing of substrates temperature.

FESEM

Figure 6 (a-f) shows the top view FESEM image of the nanostructure zinc oxide thin film. It was found that the average grain size increase when the temperature increases. It due to high temperature, the atoms has enough diffusion activation energy to occupy the correct site in the crystal lattice and grains with the lower surface energy will become larger at high temperature [14]. Table 7 summarized the average grain size of ZnO deposited at various substrate temperatures.

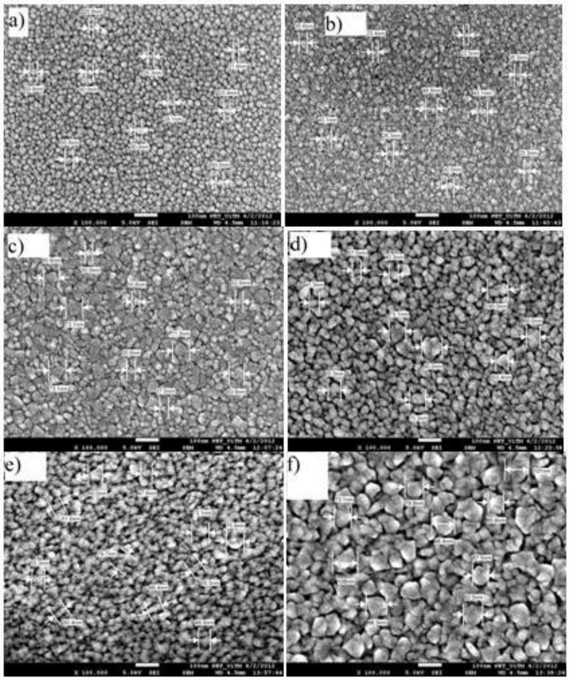

Figure 6: SEM image of nanostructure zinc oxide thin film deposited at a) room temperature, b) 100ºC, c) 200ºC, d) 300ºC, e) 400ºC, and f) 500ºC at 100k magnification and 5kV voltage

Sputtering deposition temperature	Average Grain Size of zinc oxide thin film (nm)
R.T	23.8
100ºC	24.76
200ºC	34.12
300ºC	45.56
400ºC	51.96
500ºC	71.25

Table 7: Summarized of ZnO the average grain size measured by FESEM

2. Electrical Properties

I-V Measurement

Electrical properties of zinc oxide thin film were measure using two point probes. The current-voltage (I-V) curve plotted in figure 2. From the I-V curve it can be seen that the substrate temperature at 300ºC is the highest current.

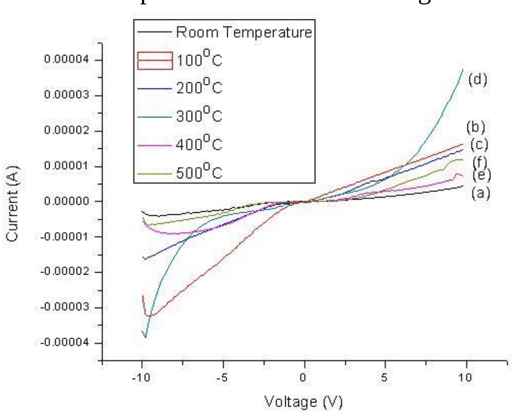

Figure 8: I-V curve of zinc oxide thin film deposited at a) room temperature b) 100ºC c) 200ºC d) 300ºC e) 400ºC f) 500ºC

The resistivity and conductivity that calculated from the I-V curve is plotted in figure 9. It can be seen that the resistivity decrease with increasing of substrate temperature which in turn that the thin film more conductive with increasing substrate temperature. The decrease of resistivity with substrate temperature is due to the enhancement of thin film crystalline, carrier concentration and carrier mobility [15].

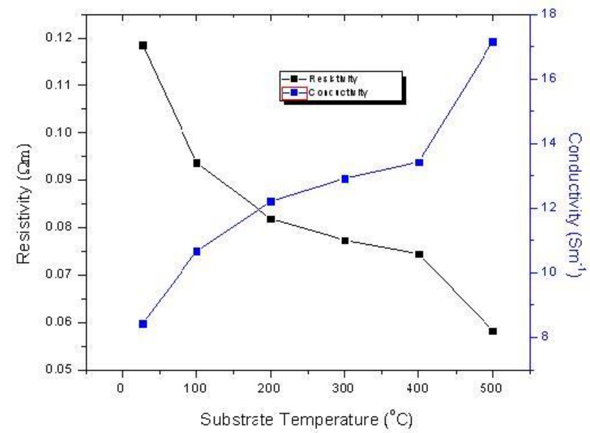

Figure 9: Resistivity and conductivity of ZnO thin films with increment of deposition temperature

3. Sensitivity

The sensitivity the calculated from equation 5 was plotted in figure 10. The substrate temperature at room temperature is higher sensitivity that is 94.5% and the lowest sensitively is 53.1% at temperature 500ºC. Due to the large surface area to volume ratio of the particles, the exposed particles at room temperature increase [9].

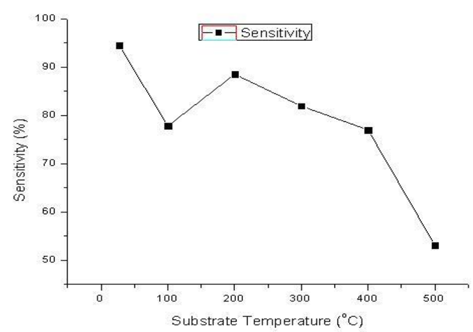

Figure 10: Sensitivity of ZnO thin films with increment of deposition temperature

IV. CONCLUSION

In conclusion nanostructures zinc oxide thin film has been deposited on the thermally oxidized p-type Si using RF magnetron sputtering. FESEM observation shows that the grain size increase when the temperature increases and the film thickness is decrease with increasing substrate temperature. The resistivity decrease with increasing of substrate temperature which in turn that the thin film more conductive with increasing substrate temperature. The highest sensitivity towards ammonia gas was recorded at room temperature substrate temperature.

ACKNOWLEDGMENT

Alhamdulillah, the author thanks to supervisor PM Dr Mohamad Rusop Mahmood, master student Samsiah Ahmad (tutor), family, friends, all staff and members of NANO-ElecTronic Centre (NET), Faculty of Electrical Engineering, and Universiti Teknologi MARA (UITM) for their support, guidance, advice and criticism in completing this project.

REFERENCES

[1] Kumico Miyazaki, Nazrul Islam (Department of Innovation, Graduate School of Innovation Management, Tokyo Institute of Technology)," *Nanotechnology systems of innovation—An analysis of industry and academia research activities*", Technovation 27, 661–675, 2007.

[2] Sharul Ashikin Binti Kamaruddin (Faculty of Electrical and Electronics Engineering, Universiti Tun Hussein Onn Malaysia)," *Zinc oxide nanostructure: The effect of deposition parameters on the electrical properties using sol-gel method*", Disember 2008.

[3] M.Y. Faizah, A. Fakhru'l-Razi, R.M. Sidek2, A. G. Liew Abdullah (Dept. of Chemical and Environmental Engineering, Universiti Putra Malaysia)," *Gas sensor application of carbon nanotubes*", International Journal of Engineering and Technology, Vol. 4, No. 1, 2007, pp. 106-113.

[4] S. Mridha and D. Basak (Department of Solid State Physics, Indian Association for the Cultivation of Science, Jadavpur, Kolkata)," *Effect of thickness on the structural, electrical and optical properties of ZnO films* ", Materials Research Bulletin 42, p-p 875–882, 2007

[5] S. S. Shariffudin, N. Z. Zakaria, S. H. Herman and M. Rusop (NANO-ElecTronic Centre, Faculty of Electrical Engineering, Universiti Teknologi MARA)," *Effect of Deposition Temperature on the Characteristics of Zinc Oxide Nanoparticles Thin Films Deposited by Thermal Chemical Vapor Deposition* ",2011 International Conference on Electronic Devices, Systems and Applications (ICEDSA), p-p 272-275, 2011.

[6] B.Rajesh Kumar and T. Subba Rao (Department of Physics, Sri Krishnadevaraya University)," *Effect of substrate temperature on structural properties of nanostructured zinc oxide thin films prepared by reactive dc magnetron sputtering* ",Journal of Nanomaterials and Biostructures, Vol. 6, No 3, p. 1281-1287, July - September 2011.

[7] T. Shishiyanu, S. Shishiyanu, 0. Lupan, V. $ontea, A. Bragorenco (Department of Microelectronics and Semiconductor Devices, Technical University of Moldova)," *Novel zinc oxide nanostructured thin films for volatile organic compounds gas sensors* ", IEEE novel, p-p 201 – 204, 2006.

[8] Chennupati Jagadish and Stephen J.Pearton," Zinc Oxide Bulk, Thin Film and Nanostructures: Processing, Propeties and Applications," First Edition 2006.

[9] M. Z. Sahdan, s. A. Kamaruddin, M. H. Mamat, z. Khusaime, U.M. Noor, Hashim Saim, A. Z.Ahmed, S. Abdullah, M. Rusop (Faculty of Electrical and Electronic Engineering, Universiti Tun Hussein Onn Malaysia),"*The Effect of Annealing Temperature on the Electrical and Optical Properties of Nanostructured ZnO for UV Sensing Applications*", leSE 2008 .Proc., p-p 571-575, 2008.

[10] Nickolette Roney, Fernando Llados, Susan S. Little, David B. Knaebel," *Public health statement*", toxicological profile for ammonia, p-p 1-10, 2004.

[11] World Health Organization," *Ammonia in Drinking-water*", Guidelines for drinking-water quality, 2nd edition Vol. 2, p-p 1-4, 1996.

[12] A. Abd Halim, H. Hashim , M. Rusop, M. H. Mamat and A. S. Zoolfakar," Study on Electrical Properties of Zinc Oxide Thin Film", IEEE Conference on Innovative Technologies, p 123-126,2008.

[13] G.Anil Kumar, M.V.Ramana Reddy, Katta Narasimha Reddy," Effect of substrate temperature on structural and optical properties of nanostructured ZnO thin films grown by RF magnetron sputtering", IEEE, p 56-60, 2011.

[14] Kwang-Sik Kim, Hyoun Woo Kim, Chong Mu Lee," Effect of growth temperature on ZnO thin film deposited on SiO2substrate", Materials Science and Engineering B98, p-p 135-139, 2003.

[15] A. Mosbaha, M.S. Aidaa," Influence of deposition temperature on structural, optical and electrical properties of sputtered Al doped ZnO thin films", Journal of Alloys and Compounds 515, p-p 149– 153, 2012.