Electrical Properties of Nanostructured Zinc Oxide Thin Films Deposited at Various RF Power by Magnetron Sputtering Method for Ammonia Gas Sensor Application

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***Abstract*— Nanostructured zinc oxide were deposited on thermally oxidized p-type silicone with various RF power by magnetron sputtering method. The surface morphology were characterize using field effect scanning electron microscope (FE-SEM). The results demonstrate the grain size increase with higher RF power. The thickness of the thin films were measured using Dektak 150 Surface Profiler and the result shows that the film thickness were higher as the RF power increase. It was found that the zinc oxide deposited at 300W gives the highest sensitivity.**

***Keywords*— Nanostructured; Zinc oxide; Magnetron sputtering**

I. INTRODUCTION

Nowadays, metal oxide thin films have been used widely in many applications including gas sensing device, fuel cells and solar energy. Zinc oxide has received a considerable attention due to it many advantages such as cheap and abundant raw materials, possible large coating, high stability in hydrogen plasma, electrical conductivity modified by appropriately doped or post-annealing, nontoxic and easy to fabricate. There is a number of techniques such as sol-gel [1], pulse laser deposition [2], reactive magnetron sputtering [3], chemical vapor deposition [4], can be used in the fabrication of zinc oxide thin film. Magnetron sputtering technique has received a great interest because of its advantage for thin film growth, such as relatively low temperature, good interfacial adhesion to the substrate and high packing density of the growth film. High operation temperature is one of the limitations to produce commercial gas sensor. That is why there is a need to produce nanostructured zinc oxide because nanostructured material produce a high surface to volume ratio [5,6], thus leads to lower operating temperature [7]. Ammonia is one of industrial gas which is very hazardous that can cause pollution to the environment as well as toxic for human [8]. Therefore, the detection of ammonia gas leakage is important. In this project, we prepare the zinc oxide thin films using magnetron sputtering method under various RF power (50 to 300W) for ammonia sensor applications. We investigate the effect of RF power on the structural and electrical properties of zinc oxide thin film. The sensitivity of the sample under ammonia gas also has been studied.

II. METHODOLOGY

A. Cleaning The Substrates

The cleaning process is the most important part to minimize the defects in this whole process. Therefore all the substrate surface is considered contaminate and it must be cleaned and dry. There are several chemicals use in the cleaning process such as acetone, methanol and de-ionized (DI) water. The substrates were sonicated using ultrasonic bath for each of the chemical for 10 minute. Then the substrates were rinse using hydrofluoric acid with the ratio of 1:10 of DI water. Lastly, the substrates were dry using argon gas.

B. Thermal Oxidation

To grow a silicone oxide layer on the top of the substrates, thermal oxidation process were conduct using high temperature furnace HV-GSL1700X at the temperature of 1000°C. The oxygen flow rate was set to 1L/min.

C. Deposition of Zinc Oxide Thin Film

In this project, we used magnetron sputtering method to deposit the zinc oxide thin films. In order to investigate the effect of the various RF power on the electrical properties of zinc oxide thin films, a series of the thin films were deposited on p-type silicon substrates at various RF power (50, 100, 150, 200, 250 and 300W). The magnetron sputtering was carried out in 45 sccm an argon gas atmosphere by supplying 50-300W RF power. The substrates temperatures were maintained at room temperature, the thickness of the films were controlled by the sputtering time.

D. Annealing

The annealing process is conducted using HV. GSL1700X high temperature furnace at 500°C for 1 hour with the oxygen flow rate was set to 1L/min.

E. Deposition of Metal Contact

A thin layer of aluminum metal contact was deposited on top of the nanostructured zinc oxide thin films by electron beam thermal evaporation. The thickness of the aluminum metal contact is 60nm.

F. Electrical Characterization

The electrical characterizations of the deposited thin films were conducted using two point probe method with applied voltage of -10V to 10 V.

G. Sensitivity Measurement

The schematic diagram for the sensitivity measurement is shown in Fig. 1. The sensor has been characterized at room temperature using simple NH_3 sensing measurement system. The ammonia solution was heated at 50˚C to produce NH_3 gaseous and the flow rate of carrier gas (Argon) is 300ml/min at 1bar while the voltage set from -10 to 10 V. The sample box and solution container were sealed to prevent ammonia leakage.

H. Physical Characterization

The surface morphology of the deposited thin films were characterized using JOEL JSM-7600F scanning electron microscope at 100,000x magnification with accelerating voltage of 5kV and the spacing between sample and scope (WD) of 4.5mm. The thickness of the prepared thin films were measured using Dektak 150 Surface Profiler.

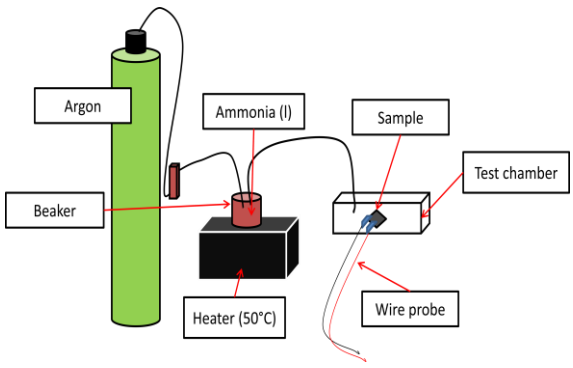

Fig.1 The arrangements of equipment for sensitivity measurement

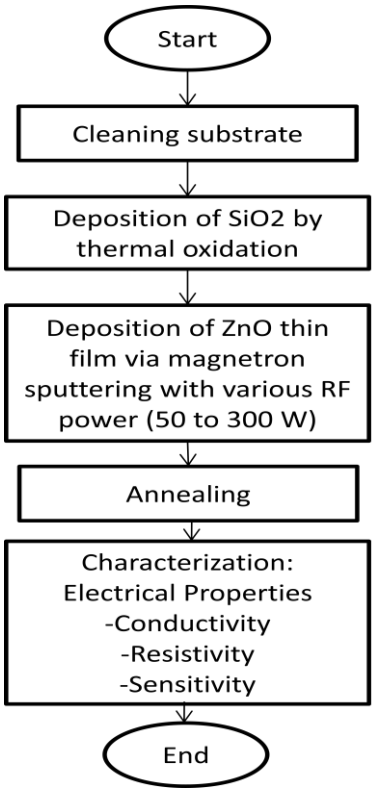

Fig.2 Process flow diagram of the methodology

III. RESULT

The surface morphologies of the nanostructured zinc oxide thin films deposited with various RF power were characterize by FE-SEM. It was found that with an increase of RF power, the grain size increase shown in Fig.3. This is because of the density of plasma during the physical vapor deposition process (PVD) increase as the sputtering power increase. The higher density of plasma will bombard down more and larger zinc particles from the target, which then react with argon to form bigger zinc oxide particles on the substrate [9]. As shown in Fig.3, the grain size is in nano scale and consists of small and uniform particle averagely around 26nm for RF power 50W, 30nm for RF power 100W and 49nm for RF power 150W. While for sputtering power of 200W, 250W and 300W shows the combination of both smaller and bigger size of particles averagely around 44nm, 50nm, 106nm for RF power 200W, 250W and 300W. The summary of average grain size variation as a function of RF power is shown in table 1.

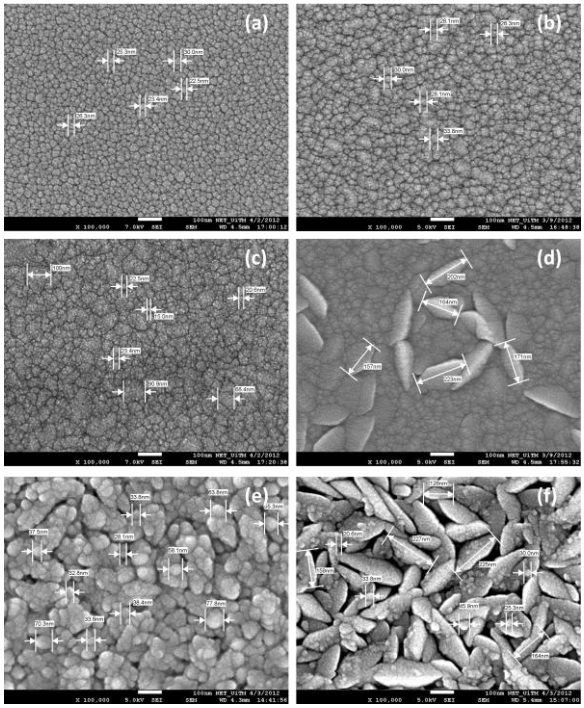

Fig.3 FE-SEM images of the zinc oxide films on Si with different RF power: (a) 50W, (b) 100W, (c) 150W, (d) 200W, (e) 250W and (f) 300W at 100k magnification and 5kV supply

TABLE 1
The average grain size of zinc oxide thin film deposited at various RF power.

RF power	Average grain size
50W	26 nm
100W	30 nm
150W	49 nm
200W	44 nm
250W	50 nm
300W	106 nm

Fig.4 showed the relation between the RF power and thin film thickness measured by surface profiler. It can be found that the thickness of zinc oxide thin film increases with the increasing RF power. When the RF power increase, more zinc atoms will be generated by sputtering and the probability of the zinc atoms to arrived on the substrate is higher. This indicates that a higher RF power will result in a higher deposition rate for zinc oxide [10].

The current voltage (I-V) of nanostructured zinc oxide thin film deposited with various RF power is shown in Fig.5. It was found that the thin film exhibit ohmic behavioral. The I-V measured for 50W, 100W, 200W and 300W is very small compared to 150W and 250W. The highest current density was recorded for the sample deposited at 250W.

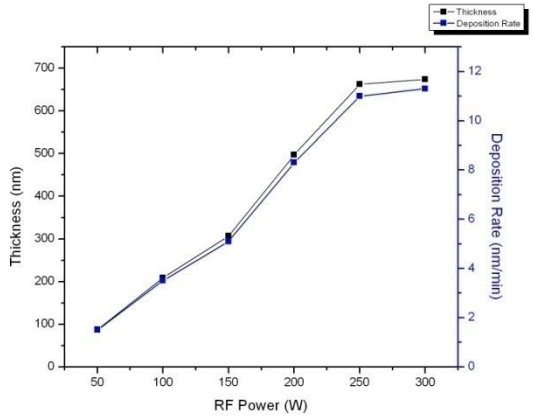

Fig.4 Relation between RF power, thin film thickness and deposition rate

The conductivity and resistivity of the nanostructured zinc oxide were shown in Fig.6. The resistivity (ρ) and conductivity (σ) is derived from the I-V result using equation 1 and 2:

$$\rho = R\left(\frac{wt}{l}\right) \qquad (1)$$

and

$$\sigma = \frac{1}{\rho} \qquad (2)$$

Where R is the resistance, w is the width on the metal contact, t is the thickness of the thin film and l is the length between metal contact. From the figure, we can find that the conductivity decrease while the resistivity increases with the increase of RF power from 50W to 300W. It can be seen from FE-SEM image in Fig.3 suggest that the conductivity of the nanostructured thin films is affceted by the nanostructure and uniform grain size. The dense nanostructure seems to be helpful to electron conduction [11]. A homogenous distribution of grains with a good crystaline quality results in a higher carrier mobility, and therefore a higher conductivity [12]. As the thin film gets thicker, it will yield low carrier mobility. Low carrier mobility will occur in thick thin film due to collision of electrons. Very thick thin film will also decrease the conductivity of a thin film [13]. The thin film thickness is shown in Fig.4.

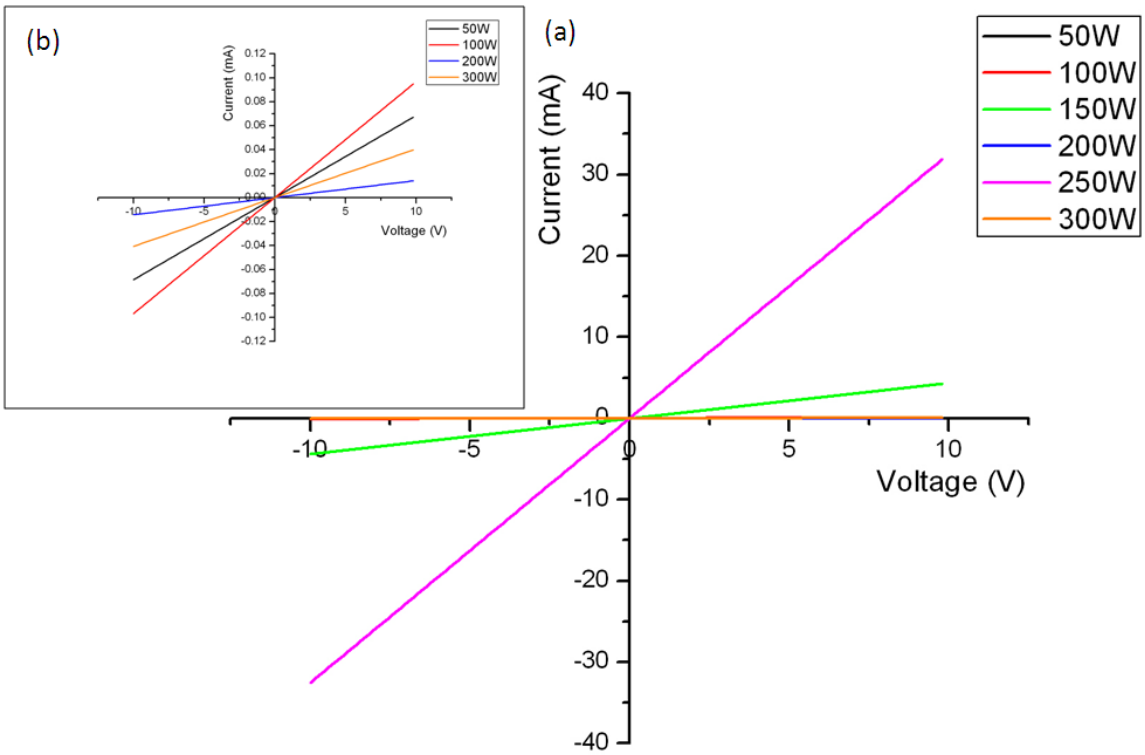

Fig.5: (a) I-V characteristic of nanostructured zinc oxide. (b) Zoomed figure for 50W, 100W, 200W and 300W

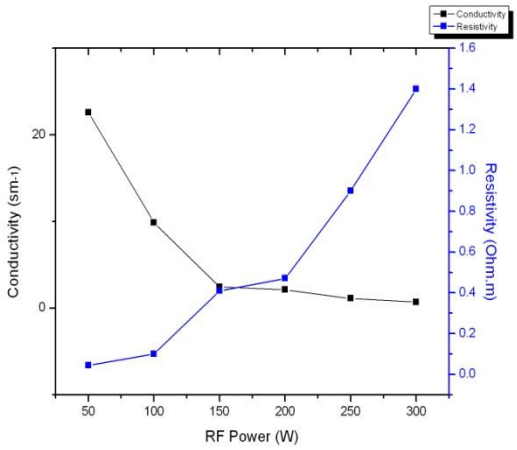

Fig.6 Relations of conductivity and resistivity of nanostructured zinc oxide with various RF power

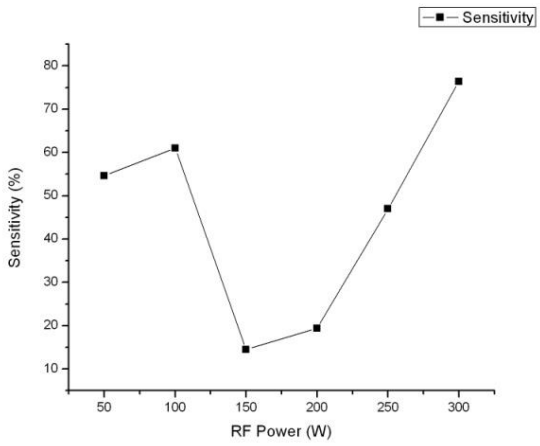

Fig.7 Sensitivity of the nanostructured zinc oxide

The sensitivity of the gas sensor is calculated using equation 3:

$$S = \frac{Ra - Rg}{Ra} X\ 100 \qquad (3)$$

Where Ra is the resistance at ambient environment and Rg is the resistance under the presence of ammonia gas. The sensitivity of gas sensors is shown in Fig.7. As we can see from the figure, substrate deposited at 300W RF power has the highest sensitivity that is at 76%, followed by 100W, 50W, 250W, 200W and lastly 150W at the value of 15%. The high sensitivity of the nanostructured zinc oxide is due to the large particle as shown in Fig.3(f) that provides high surface area for gas-solid reaction, while the moderate sensitivity can be attributed to tightly packed crystallites with less porosity [14].

IV. CONCLUSIONS

In conclusion, we have successfully deposited nanostructured zinc oxide with various RF power by magnetron sputtering method. The thickness and deposition rate increases with the increased of RF power. FE-SEM result shows that the grain size increases as the RF power increases. The zinc oxide deposited at 300W shows highest sensitivity which is 76%.

Moreover, we would like to recommend to deposit nanostructured SnO2 in exchange of the nanostructured ZnO for ammonia gas sensor application. This is because ZnO is less popular compared to SnO2 because of its high operating temperature. Thus, there is a high possibility that a nanostructured SnO2 will result a low operating temperature ammona gas sensor with batter sensitivity than a nanostructured ZnO.

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