THE INFLUENCE OF PLATINUM DOPANT ON THE CHARACTERISTICS OF SnO_2 THIN FILM FOR GAS SENSOR APPLICATION

Tjipto Sujitno, Sudjatmoko
Center for Research and Development of Advanced Technology
National Nuclear Energy Agency
Jl. Babarsari, Kotak Pos 6101 Ykbb
Yogyakarta, 55281, Tel. (0274) 488435, fax : (0274) 487824

ABSTRACT

THE INFLUENCE OF PLATINUM DOPANT ON THE CHARACTERISTICS OF SnO_2 THIN FILM FOR GAS SENSOR APPLICATION. Doping of platinum on tin dioxide (SnO_2) thin film for gas sensor application has been carried out using ion implantation techniques. The SnO_2 thin film has been deposited using dc sputtering method at the conditions; operating pressure $5x10^{-2}$ torr, anode-cathode voltage 2.0 kV, substrate temperature 200^0C and deposition time one hour. While the Pt ion implantation process were carried out at energy 60 keV and ion doses were varied. From scanning electron microscope (SEM) observation, it was found that SnO_2:Pt thin film which was deposited by those parameters has a fine morphology with the grain size of thin film was in order of 0.7 – 1.0 μm and thickness 4.16 μm. From crystal structure analysis using XRD it was observed that the crystal planes of SnO_2:Pt were (110), (101), (200), (211), (300), and (112) . From energy dispersive X-rays analysis (EDX) coupled with SEM, it was found that the chemical composition of SnO_2:Pt thin film were 66.12%-at O, 1.23 %-at Si, 0.12 %-at Pt and 32.53 %-at Sn. It was also found that the influence of platinum dopant on SnO_2 thin film can reduce significantly the resistance of thin film and from response time and sensitivities measurement showed that for every dose variation for different tested gas has a different respons time and sensitivities (no a specific pattern).

Keywords : SnO_2:Pt thin film, gas sensor, sensitivity, and response time, ion implantation, sputtering .

INTRODUCTION

The air is admixture of gases, depending on the environment, it may contain various chemical pollutants, e.g SO_x, NH_3, H_2S, CO or volatile organic compounds. Some of these pollutants are either explosive (like methane) or highly toxic (like carbon monoxide). The others cause disturbances in human or animal body[1,2].

With the development of engineering and industries, our air more polluted. Living in contemporary industrialized world requires the protection against the influence of this hazardous substance, what induces the need for continuous monitoring of air pollutant in the environment, in the factories, in technological installation and on the specified compounds. However the precise instrumental analyses such as gas chromatography are very expensive and time consuming[3].

The control system should allow continuous reading for the concentration of gases in a quantitative and selective way. The system should be cheap, and exhibit such virtues as high sensitivity and selectivity, fast response and long term stability. In addition to warning against air pollution and steering of technical processes requires such gas sensitive system. An example is provided by the combustion engine in cars. The exhaust gases have to be checked for toxic admixtures like carbon monoxide and nitrogen oxygen compounds.

Since the demonstration almost 50 years ago[4,5], that the adsorption of gas on the surface of semiconductor can bring about a significant change in the electrical resistance of the material, there has been a sustained and successful effort to make use of this change for purposes of gas detection[6]. Detection of toxic and flammable gases is a subject of growing importance in industrial environments.

The achievement in microelectronics provided the development and massive production of low cost semiconductive sensors based on gas sensitive materials changing its resistance and/or impedance when hazardous substances appear in the air.

Simple metal oxides such as ZnO, WO_3, TiO_2, Fe_2O_3, Al_2O_3, Y_2O_3 and SnO_2, are well known for their high sensitivity to change in the surrounding gas atmosphere. The growing number of papers[7-10] reporting on the successful application of these oxides in gas sensing devices shows the important role they play in the gas sensor field. Eventually the tin oxide became the dominating gas sensitive and widely used as gas sensors due to their high sensitivity in the precense of small amount of some gases of interest viz. carbon monoxide, ethanol, methanol etc. Allied to this advantage is the simple design, robustness, fast response and the possibility of miniaturization of the devices[11]. Most of the commercial gas detectors for hydrogen, methane and carbon dioxide available at present make use of SnO_2. They operate at moderate temperatures 300 – 400^0C, and are considered as a "surface sensors", because the gas-solid interactions leading to the physical adsorption modify electron/hole density in a relatively shallow region near the surface[12-14].

When a SnO_2 semiconductors film is exposed to air physisorbed oxygen molecules received electrons from the conduction band of the film and change to O^- ads or O^{2-} ads species. These adsorbed molecules form an electron depletion layer just below the surface of SnO_2 particles and forms a potential barrier between particles; consequently the SnO_2 films become highly resistive[13]. The lowering of the potential barrier takes place when the adsorbed oxygen species are exposed to reducing gases, resulting in the increased conductance measured under specific gases depend on many parameters such as intrinsic resistance, grain size, grain boundary barriers and detection temperature.

Doping with the noble metals such as Pt, Pd, and Au can raise the adsorption activity of the semiconducting oxides. These metals form cluster on the oxide surface, promoting adsorption and dissociation of reducing gases. In particular, Pd, Pt and Au cluster reduce the work function and the activation energy of surface reaction. These noble metals also have a significant influence on the electrical properties, microstructure, and grain size[14]**.** Tin oxide films can be prepared by a number of techniques including spray pyrolysis, sputtering chemical vapor deposition, evaporation and recently the sol-gel process has been proposed as a new technique for preparing gas sensor devices[15]. In this work, we report the fabrication and characterization of SnO_2 thin film prepared using D-C sputtering technique and implanted with platinum (Pt) using ion implantation technique

METHODOLOGY

Steps of this research are sample preparation, sputtering process, implantation process, annealing process, fabrication of contact, characterization and data analysis.

Sample preparation

Sputtered target with 60 mm in diameter and 3 mm thickness made of 30 g SnO_2 powder, the powder are mixed with alcohol as a binder until form a batter and than this batter is poured into dies and pressed for 16 ton. After that, this disc was annealed for 900^0C. As a substrate, we use 10 mm x 15 mm preparat glass.

Sputtering, implantation, and annealing process

Deposition of SnO_2 thin film on glass substrate and fabrication of silver (Ag) contact were carried out using D-C sputtering technique, while the doping of platinum (Pt) into SnO_2 thin film was used ion implantation technique using 150 keV/2 mA ion implanter. The condition of sputtering process are; operating pressure $5x10^{-2}$ torr, anode-cathode voltage 2.0 kV, substrate temperature 200^0C and deposition time one hour. While the Pt ion implantation process were carried out at energy 60 keV and ion doses were varied. The objective of the annealing process is to reduce the internal stress and radiation damage due to the implantation process. For the SnO_2 thin film the appropriate annealing temperature is 300^0C – 400^0C.

Characterization of the SnO_2 thin film

The main characterization of gas sensors usually requires two kinds of measurements; (1) time response to a given gas concentration, measured for the sensor operating at constant temperature, (2) determination of the

working temperature at which the sensor reaches the maximum sensitivity to a given gas at the constant concentration. Besides these characterization, some times characterization of microstructure, crystal structure, and chemical composition are very needed, because there are strong correlation between macro properties (time response, working temperature, sensitivity) and micro properties (microstructure, crystal structure, and chemical composition)

RESULTS AND DISCUSSION

Determination working temperature

One of the disadvantages of the semiconductive sensor is that they operate at moderate temperatures 300–400^{0}C. The operating temperature is defined as temperature where the resistance of the sensor reaches the constant value, the changing of resistance is just only influenced by the presence of amount of some gases of interest. The operating temperature of SnO_2 and SnO_2: Pt are presented at Figure 1 and Figure 2.

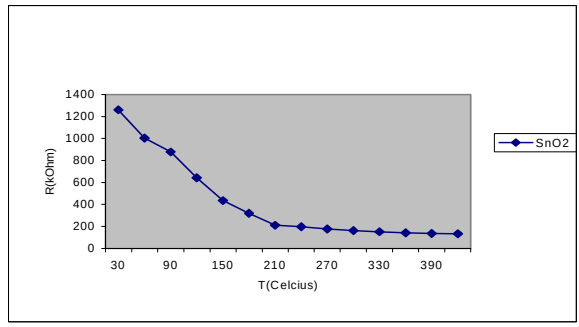

Fig. 1. Effect of temperature on the resistance of SnO_2 thin film.

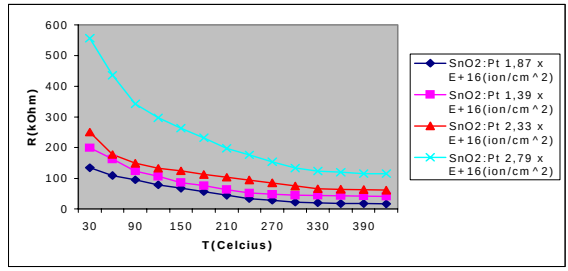

Fig. 2. Effect of temperature on the resistance of SnO_2 doped by platinum for various ion dose at energy 60 keV.

From Figure 1 shown that for undoped SnO_2 thin film, starting temperature in order of 330^0 C, its resistance reaches almost constant value, there is no changing in resistance if the temperature is increased. Starting

from this temperature can be called as the operating temperature of the sensor. The phenomenon of the constant value of resistance of SnO_2 thin film can be explained as follows; during heating of thin film, electrons in valence band get thermal energy addition, consequently the electrons in valence band move easily to conduction band and the resistance of thin film reduce.

Figure 2 shows the effect of temperature on the resistance of SnO_2 doped by platinum for various ion dose at energy 60 keV. During the film is exposed to reducing gases such as NO_2, O_2 and CO_2, oxygen molecules receive electrons from the conduction band of the SnO_2 film and change to O^- or O_2^- ads species. Theses adsorbed atom or molecules form an electron depletion layer just bellow the surface of SnO_2 and forms a potential barrier between particles consequently the SnO_2 thin film become highly resistivity, on the other hand the conductance of SnO_2 decreases. When the film is exposed to oxidizing gases such as CO, H_2 and CH_4, these gases adsorbs O atoms from the surface of the film and create an oxygen vacancy. These vacancies causes two electrons of thin film to be free. Consequently the conductance of the thin film increases[3,6,11]. After these films implanted with platinum ions for various dose at energy 60 keV, the resistance and the operating temperature of the film reduce. This phenomenon can be explained as follow; the addition of platinum Pt can raise the adsorption (oxygen molecules) activity of the semiconducting oxides. This metal form cluster on the oxide surface, promoting adsorption and dissociation of reducing gases such as NO_2, O_2 and CO_2[9]. In particular Pt cluster reduce the work function and the activation energy of surface reaction. Besides that, ions of platinum occupy energy level below conduction band and behave as an activator, consequently electrons move easily move to conduction band, so that the resitance of thin film reduce.

Effect of annealing temperature

The effect of annealing temperature on SnO_2 thin films implanted with platinum for various dose at energy 60 keV is presented at Figure 3.

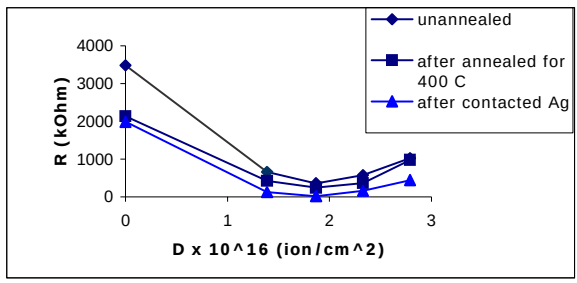

Fig. 3. Effect of annealing temperature on SnO_2 thin films implanted with platinum for various dose at energy 60 keV.

Figure 3 showes that the resistance of unannealed, after annealed for 400^0C and after coated/contacted with silver (Ag) of SnO_2 thin film doped with platinum (Pt) for various ion dose at energy 60 keV. From Figure 3 shown that the resistance of thin films which originally 3.42 MΩ after implanted with platinum ion for ion dose 1.39 x 10^{16} ion/cm^2, 1.87 x10^{16} ion/cm^2, 2.33 x10^{16} ion/cm^2, and 2.79 x10^{16} ion/cm^2 reduce to 658 kΩ, 356 kΩ, 574 kΩ, and 1023 kΩ respectively. After annealing process for 400^0 C the resistance also reduce to 2.13 MΩ, 424 kΩ, 242 kΩ, 365 kΩ, and 978 kΩ. Giving silver contact also reduce the resistance of thin film to 1.98 MΩ, 203,8 kΩ, 148,5 kΩ, 165,1 kΩ, and 441 kΩ respectively. Based on Figure 3, it can be concluded that, the effect of platinum doping and annealing process can reduce the resistance of the thin films.

Sensitivity of the sensor

The sensitivity of the gas sensor is defined as the capability of the sensor to respond the presence of a given gas concentration. Matematically, the sensitivity S is defined by the formula;

$$S = \frac{\Delta R_g}{R_n} = \frac{R_g - R_n}{R_n} \quad (1)$$

for reductor gas

and

$$S = \frac{\Delta R_g}{R_n} = \frac{R_n - R_g}{R_n} \quad (2)$$

for oxidator gas

where R_g and R_n is the resistance of the sensor after and before passing the gas and reaches the saturation. The Sensitivities of SnO_2 and SnO_2 Pt thin film for various gas tested HCl, CH_3OH, and NH_3 at working temperature 320^0C and 380^0C are presented at Fig. 4 and Fig.5.

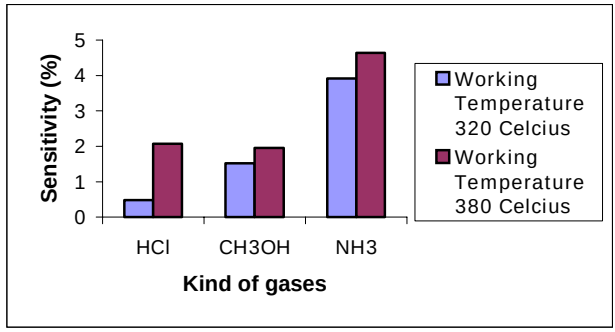

Fig. 4. Sensitivities of SnO_2 thin film deposited using dc sputtering method at the conditions; operating pressure $5x10^{-2}$ torr, anode-cathode voltage 2.0 kV, substrate temperature 200^0C and deposition time one hour for various gas tested HCl, CH_3OH, dan NH_3 working temperature 320^oC and 380^oC.

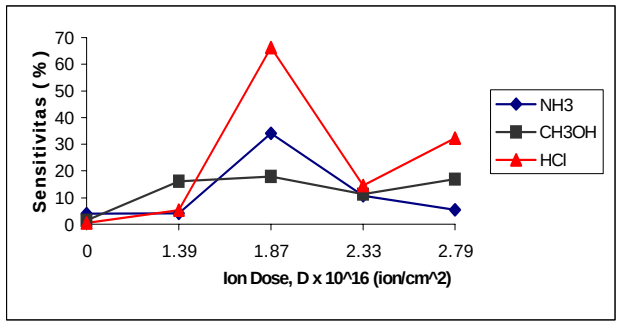

Fig.5. Sensitivities of SnO_2:Pt thin film for various gas tested NH_3, CH_3OH, and HCl at working temperature 320^0C and gas volume 0,769 ($x10^4$) ppm.

From Fig. 4 shown that with the increasing of working temperature 320^0C to 380^0C the sensitivity of the films to HCl, NH_3 and CH_3OH increases (more sensitive). For various of gas tested and for working temperature 320^0C, the highest sensitivity around 4.64 % is response to NH_3 gas tested, while the lowest sensitivity around 1.96 % is response to CH_3OH. From Fig. 5 shown that after implanted with platinum (Pt) for various ion dose at energy 60 keV, the sensitivity of the thin film implanted for ion dose ion 1.39 x 10^{16} ion/cm^2, the highest sensitivity is response to CH_3OH gas tested (16.14%) and the lowest sensitivity is response to NH_3 (4.12%) gas tested. At ion dose $1.87x10^{16}$ ion/cm^2, the highest sensitivity is response to HCl (66.38%) and the lowest sensitivity is response to CH_3OH (17.93%). At ion dose $2.33x10^{16}$ ion/cm^2, the highest sensitivity is response to HCl (14.61%) and the lowest

sensitivity is response to NH_3 (10.81%). At ion dose 2.79 x 10^{16} ion/cm^2, the highest sensitivity is response to HCl (32.30%) and the lowest sensitivity is response to NH_3 (5.41%) gas tested. From these data, it can be concluded that the implantation of platinum with ion dose in order of 1.87xx 10^{16} ion/cm^2 will give highest sensitivity for three of gas tested. From these data, it also can be concluded that for every ion dose variation and for difference tested gas has a difference sensitivities (no a specific pattern). In other hand this sensor can be developed as a specific sensor.

Response time of the sensor

Response time of the sensor defined as the time needed for the sensor to reach 90 % of the final signal for a given concentration of the tested gas. In this experiment, the tested sensor has resistance around (1.3460,02) MΩ, concentration of the gas tested is 0.769 x10^4 ppm, working temperature is 320^{0}C and 380^{0}C. Response time of SnO_2 and SnO_2: Pt thin films are presented at Fig. 6 and Fig.7.

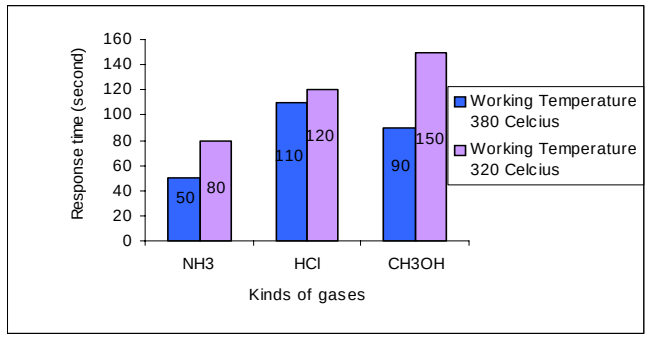

Fig. 6. The response time of SnO_2 thin film to NH_3, HCl, and CH_3OH (methanol) for working temperature 320^{0}C and 380^{0}C.

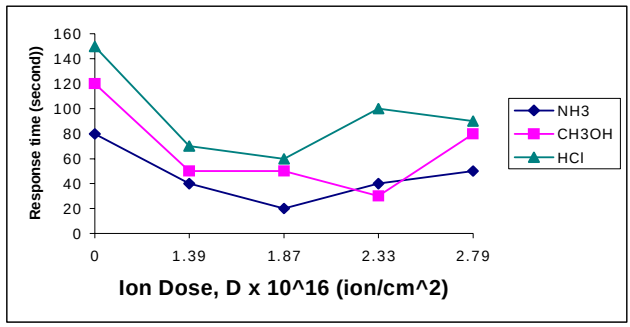

Fig. 7. Effect of platinum ion dose on the response time of SnO_2 thin film at working temperature 320^{0}C.

Response time of SnO_2 thin film at working temperature 320^oC to NH_3, HCl and CH_3OH gas tested is 80 second, 120 second, and 150 second. While the response time of SnO_2 thin film at working temperature 380^oC to NH_3, HCl and CH_3OH gas tested is 50 second, 110 second, and 90 second. At the lower working temperature the SnO_2 thin film shows the longer response time compared to response time operated at working temperature 380^oC. In this phenomenon may be the electrons in valence band is still not enough energy to move to conduction band and react with gas tested.

From Figure 7 shown that the effect platinum doping can increase the response time of the sensor. For example; the response time of undoped SnO_2 thin film to NH_3 gas tested is 80 second, after this film doped with platinum at ion dose 1,87 x 10^{16} ion/cm^2 , the response time decrease to 20 second. This dose as an optimum dose that give a fastest response time for sensor in responding presence of NH_3 gas. At ion dose 1,39 x 10^{16} ion/cm^2, the fastest response time in order of 40 second reached if the sensor is used to detect of NH_3 gas, and the longest response time in order 70 second, if the film is used to detect the HCl gas. At ion dose 1,87 x 10^{16} ion/cm^2, the fastest response time in order of 20 second, if the film is used to detect NH_3 gas, while the longest response time in order of 60 second, if the film is used to detect HCl gas. At ion dose 2,33 x 10^{16} ion/cm^2, the fastest response time in order of 30 second, if this film is used to detect of CH_3OH gas and the longest response time in order of 100 second if this film is used to detect of HCl gas. At ion dose 2,79 x 10^{16} ion/cm^2, the fastest response time in order of 50 second, if the film is to detect NH_3 gas and the longest response time in order 90 second, if this film is used to detect of HCl gas. From these data, it can be concluded that the increasing in ion dose does not give a determinate pattern in the response time.

The differences in response time and kinds of gas for every platinum ion dose given depend on the number of free electrons produced when the film react with oxygen atoms. If the free electrons produced small, the conductivity of the film is low, so the response time of the film is long.

XRD Analysis

Fig. 8 and Fig. 9 shows the XRD pattern of SnO_2 thin film deposited using *dc sputtering* technique for 1 hour and temperature 200^0C and XRD pattern of SnO_2 thin film deposited using *dc sputtering* technique for 1 hour and substrate temperature 200^0C and implanted by platinum ion at energy 60 keV, and ion dose 1.87 x 10^{16} ion/cm^2.

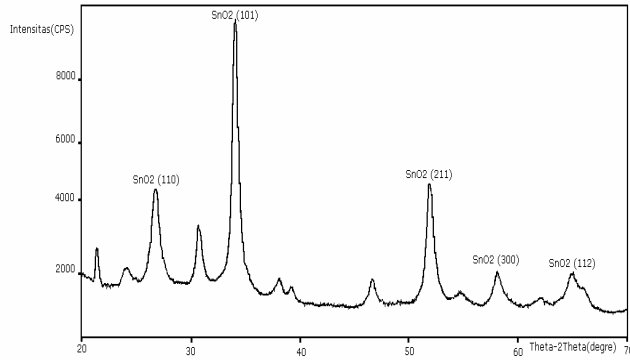

Fig. 8. XRD pattern of SnO_2 thin film deposited using *dc sputtering* technique for 1hour and temperature 200^0C.

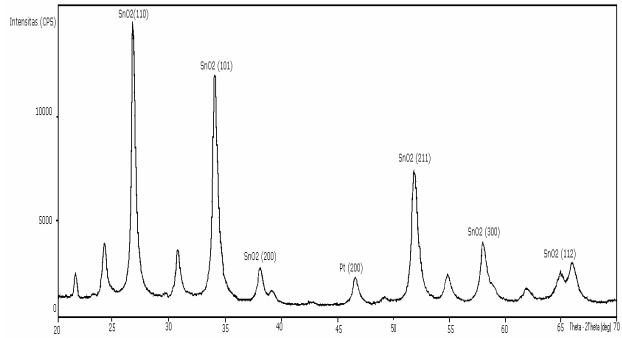

Fig. 9. XRD pattern of SnO_2 thin film deposited using *dc sputtering* technique for 1 hour and substrate temperature 200^0C and implanted by platinum ion at energy 60 keV, and ion dose 1.87 x 10^{16} ion/cm^2.

From Fig. 8 shown that X-rays spectrum of SnO_2 thin film has a number of peaks, it meant that film is polycrystalline with crystal planes (110), (101), (211), (300) and (112). From Fig.9 shown that X-rays spectrum of SnO_2:Pt thin film also has a number of peaks, it meant that the SnO_2:Pt thin film is also polycrystalline with the crystal planes l (110), (101), (200), (211), (300), (112) and (200). The presence of platinum is indicated by the planes of (200). The crystal planes can be determined by comparing the experiment inter-planar spacing d_{hkl} and relative intensity with d_{hkl} and relative intensity on JCPDS (*Joint Committee Powder Diffraction Standards*) table for SnO_2 and platinum or it can be calculated using computer program.

Microstructure of SnO_2 and SnO_2:Pt thin film

SEM (*Scanning Electron Microscope)* surface micrograph and cross-section micrograph of SnO_2 thin film and SnO_2:Pt thin film gas sensor are presented on Fig.10, Fig. 11 and Fig. 12 and 13.

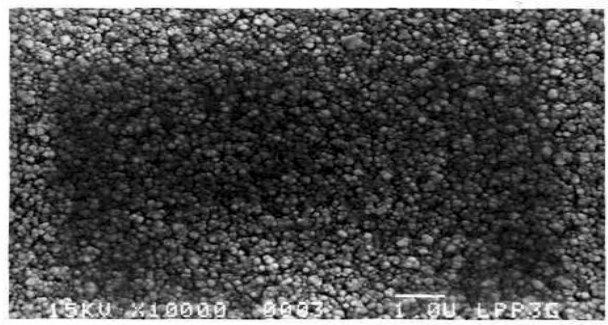

Fig. 10. Microstructure of SnO_2 thin film deposited using *dc sputtering* technique for 1 hour and substrate temperature 200^0C, magnification x 10,000.

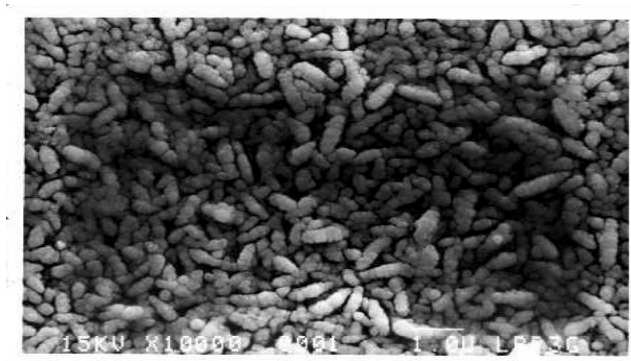

Fig.11. Microstructure of SnO_2:Pt thin film deposited using *dc sputtering* technique for 1 hour, substrate temperature 200^0C and implanted by platinum ion at energy 60 keV, and ion dose 1.87 x 10^{16} ion/cm^2, magnification x 10,000.

Compare Fig.10 to Fig 11, it can be shown that grain size SnO_2 thin film smaller than grain size of SnO_2:Pt thin film. SnO_2 thin film has average grain size in order of 0.1–0.2 μm, while the average grain size of SnO_2:Pt thin film is in order of 0.7–1 μm. The SnO_2 thin film grains look like sands and distributed homogenously. This indicates that the deposited thin film is homogen. The grain size of SnO_2:Pt thin film is bigger than grain size of SnO_2 thin film Theoriticaly, the grain size of SnO_2:Pt should be smaller, this phenomenon is caused by to the fact that during implantation process create a heat in order of 125^0 C and after ion implantation process, the SnO_2: Pt thin was annealed at 400^0C, of course, the grain size will grow.

Cross section microstructure of SnO_2 and SnO_2 implanted by platinum ion at energy 60 keV, ion dose 1.87 x 10^{16} ion/cm^2 and annealed temperature for 400^0C are presented on Fig.12. and Fig. 13.

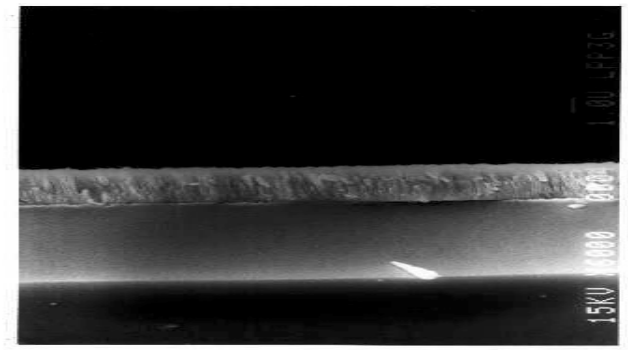

Fig.12. Cross section microstructure of SnO_2 thin film deposited using *dc* s*puttering* technique for 1 hour and substrate temperature 200^0C, magnification 600 x.

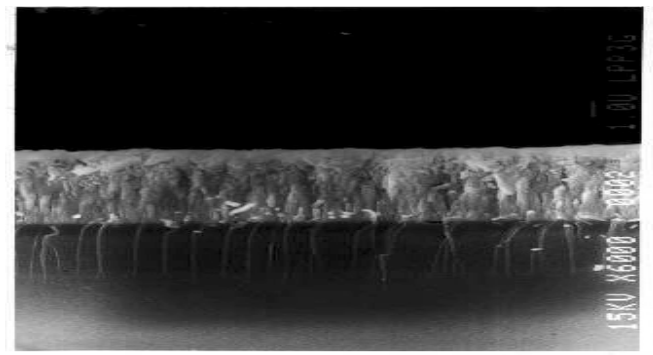

Fig. 13. Cross section microstructure of SnO_2 thin film implanted by platinum ion at energy 60 keV, and ion dose 1.87 x 10^{16} ion/cm^2 , magnification 600 x.

From Fig.12 and Fig. 13 shown that the thickness of SnO_2:Pt thin film is thicker than thickness of SnO_2 thin film. Thickness of SnO_2 thin film (Fig. 12) is in order of 1.92 μm while the thickness of SnO_2: Pt thin film (Fig.13) in order of 4,16 μm.. From The both figure are also shown that the thin films have a smooth surface, it is indicates that the surface of the thin film is distributed homogeneously.

Chemical Compositions of the thin films

The chemical composition of thin films were analysed using EDX (*Energy Dispersive X-rays Spectroscopy*) spectrometry coupled with SEM (*Scanning Electron Microscope).* The results are presented on Fig. 14 and Fig.15.

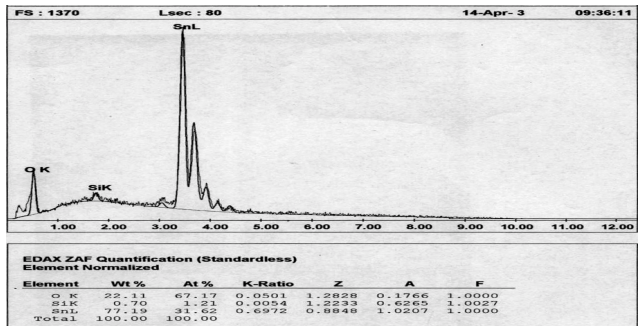

Fig. 14. Chemical composition of SnO_2 thin film analyzed using EDX. The content of Sn and O element deposited on glass substrate are 31.62 at % and 67.17 at % respectively, while the rest (1.21 at %) is Si.

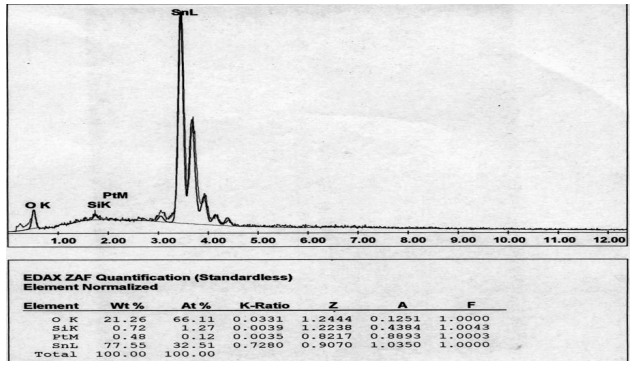

Fig. 15. Chemical composition of SnO_2:Pt thin film analyzed using EDX. The content of Sn, O and Pt element deposited on glass substrate are 31.51 at % and 66.11 at % , and 0.12 at % respectively and the rest (1.27 at %) is Si.

Fig. 14 shows the chemical composition of SnO_2 thin film deposited for 1 hour and substrate temperature 200^0C, while Fig.15 shows the chemical compositions of the SnO_2 : Pt thin film. From Fig. 14 shown that the chemical compositions of SnO_2 thin film on glass substrate are 31.62 at % Sn, 67.17 at % O and 1.21 at % Si. While chemical compositions of SnO_2 : Pt thin film are 31.51 at % Sn, 66.11 at % O, 0.12 at % Pt and 1.27 at % Si. The presence of silicon (Si) in order of 1.21 at % - 1.27 at % is caused by to the fact that in this experiment, we used glass (parts of the glass component is Si) as a substrate.

CONCCLUSION

Based on the experiments and analysis, it can be concluded that;

- The influence of platinum dopant on SnO_2 thin film can reduce significantly the resistance of thin film, the lowest resistance in order of 1485 kΩ is achieved at ion dose 1.87 x 10^{16} ion/cm^2.
- From response time and sensitivities measurement showed that for every dose variation and for differences tested gas has a different response time and sensitivities (no a specific pattern).
- From scanning electron microscope (SEM) observation, it was found that SnO_2:Pt thin film which was deposited by those parameters has a fine morphology with the grain size of thin film was in order of 0.7 – 1.0 μm and thickness 4.16 μm.
- From crystal structure analysis using XRD it was observed that the crystal planes of SnO_2:Pt were (110), (101), (200), (211), (300), and (112).
- From energy dispersive X-rays analysis (EDX) coupled with SEM, it was found that the chemical composition of SnO_2:Pt thin film were 66.12%-at O, 1.23 %-at Si, 0.12 %-at Pt and 32.53 %-at Sn.

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