Effect of Thermal Processes on Al Thin Film In The Present of Nitrogen (N_2) Gas

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Abstract ? The morphology evolution of Aluminum (Al) thin film in the present of Nitrogen (N_2) gas has been studied. The Aluminum thin film has been fabricated on Silicon (Si) substrate using Aluminum evaporation system. Then, the substrate were placed inside the furnace with the present of N_2 gas for approximately 30 minutes at certain temperature range from room temperature to 700 °C. The influence of the N_2 gas to the Al thin film in furnace were characterized by optical microscope, *Scanning Electron Microscope* (SEM), *Energy Dispersive Spectrometer* (EDS), I – V characterization and X- ray diffraction (XRD). It is found that, at above 600 °C, we observed that the colour of Al thin film was changed drastically. We expect that this is because of the formation of ALN on the Si substrate. This statement is proved by the XRD and EDS characterization results. In addition, the thin film has better resistivity than the thin film before thermal processing, which was evaluated from I – V characterization results. From the SEM images, we also found that the morphology of Aluminum thin film changed drastically for the temperature above 600 °C.

Keywords: *Aluminum thin film, Aluminum Nitrate, Nitrogen Gas, Silicon Substrate.*

INTRODUCTION

Advance material such as Beryllium Oxide [1] (BeO), Aluminum Nitrate [2] (ALN), Boron Nitrate [2] (BN), Gallium Nitrate [2] (GaN), Indium Nitrate [2] (InN) and many more other are showing many advantages to be applied in high performance materials applications due to their high mechanical strength [3], hardness properties [3] and low in weight [3]. Such resultant conditions have led this ceramic material started to be introduced in many advance applications.

AlN is a ceramic material that has been used in many advance sectors such as in military, medical, data storage, communication and many others. The material is been selected as conducting material due to its thermal conductivity value and ease of handling with no toxic. Examples of application of AlN are electronic substrate, heat sink, dielectric layers in the optical storage, optoelectronics, thin film bulk acoustic resonator (FBAR). In the electronic substrate application for high frequency operation communication based industry, the element of high thermal conductivity is very important factor to exhaust heat immediately to decrease the noise develops. The FBAR is a type of RF filter used in mobile communication which will have ALN sandwiched between two metal layers [4].

It is found that, a major disadvantage of most ceramic listed above is believed to be listed high in cost. This factor has led to a situation of limited use commercially rather for research purpose only. It is understand that, commercial ceramic are made from starting ceramic powder which will later been shaped form desire ceramic. The starting powders are often made by energy – intensity processes or by other expensive methods adapted to produce high purity starting powders [3]. Higher degree of purity will cause decrease in impurity content which will alter the total performance of the ceramic.

In this paper, the Al thin film was fabricated on the Silicon (Si) substrate and the morphology evolution of the Al thin film in present of Nitrogen (N_2) and heat on the surface of the thin film is studied. The evolutions are been characterized by optical microscope, Scanning Electron Microscope (SEM), Energy Dispersive Spectrometer (EDS), I – V characterization and X- ray diffraction (XRD). The study of the material is discussed at the end of the paper.

EXPERIMENTAL DETAILS

A fresh Si (111) substrate wafer is cleaned using dilute water (H_2O). The substrate is inserted into Physical Vapour Diffusion (PVD) chamber which contains Al foil as a metal source at the coil. The process is continued to vacuum up to 10^{-5} Torr using high vacuum system. It will consist of 45 minutes of waiting. Once the pressure meter shows desired value, the evaporation process can be begin by increasing the voltage of the coil about 30% for 5 minute (coil – dark red), then up to 60% about 10 seconds (coil – red) and then to 80% for about 90 seconds (coil – bright orange). The colour at the coil will change according to the value of voltage supplied. After 90 second at 80% voltage source, the toggle is turn back to 0% and let cool for 5 minute before the chamber is opened.

The Al thin film deposited on Si substrate is now ready to be inserted into the furnace system for further experiment. The substrate was cut to several pieces of sample to provide same fundamental thickness (Al thin film) on every sample before proceeding to next process. The furnace system is ramped up to 250°C and the N_2 gas flow is opened. Then, the furnace is ramp up with respective sample to certain parameter of temperature such as 300°C, 500°C, 600°C and 700°C. The N_2 flow is maintained at 10 bar for every section. In every condition, the N_2 is provided for approximately 30 minutes before the furnace is ramp down during the cooling period. Every sample is characterized using optical microscope, Scanning Electron Microscope (SEM), Energy Dispersive Spectrometer (EDS), I – V characterization and X - ray diffraction (XRD).

The use of optical microscope is to magnify the sample up 30X, before having a rough look on surface of the sample. The sample is been placed on the tray and by varying the focus point of the lens, the optical image of each sample are recorded.

The SEM (model of JEOL JSM – 6380 LA) can help to magnified much higher up to 2000X magnification. The system is located in *Makmal Sains Bahan*, UTHM. Sample is placed on the substrate holder and been inserted into the SEM chamber before pumping up the chamber using turbo pump. The focus of image appear on the online video of the SEM is adjusted until clear image is produced. For 500X, 1000X, 1500X and 2000X of the every sample are recorded. The SEM is equipped with EDS system that allows the user to analyze the elements exists by marking the area in square, point or circle. Majorly, the rectangular type is chosen. EDS, with the help of liquid N2 will propagates through the sample and the characterized result will appear in form of graph. Every sample will undergo 5 times of test at various different areas and every result obtain is recorded.

The X- ray diffraction (XRD) is used to detect any elements occur on the surface material. The result in form of graph is compared with the pre loaded library before assumption of material can be made. For every range of temperature, the data in form of graph is recorded. While, the I – V characterization can be used to determine the resistivity of the sample in form of voltage versus current. Every data of the sample is recorded and been analyzed.

RESULT AND DISCUSSION

The surface of the thin film with scratch using wafer forceps and without scratch is shown in the figure 1. After the process of PVD, by observation it shows that, the reflection ability of the thin film has increase. We can understand that, the element Al has diffused on the surface of the Silicon substrate. The scratch test shows that, the Al layer that enclose on the surface of the silicon wafer is not chemically bonded and easy to scratch out even using human nail.

From the test above, we come to know that, for thin film of 25 °C, it is much easy to scratch the layer of Al on the surface of Si substrate. While the sample of 600 °C, it is much harder to scratch and the resultant optical image shows the effect of scratch is much smaller than the sample of 25 °C.

On the optical microscope, the surface morphology shows very clear picture of the changes that happens on the thin film when heated to certain level of temperature in the present of N2 gas. The impurity grows drastically as the temperature parameter increases. This can be differentiated from analyzing the dots rate per area for every sample in the figure 2.

From the results, it is clearly shown that, the number of impurity (dots) have a steady increase from 25 °C to 700 °C.

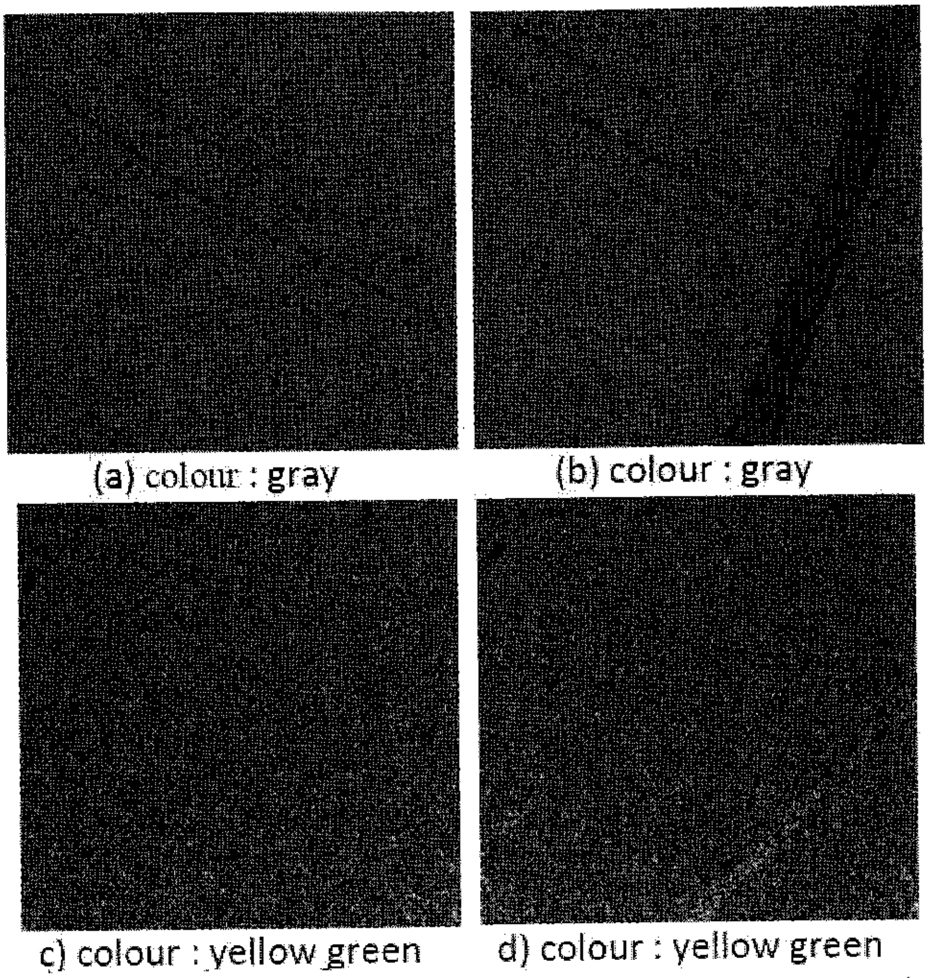


Figure 1 : The thin film of 2 different temperature of 25 °C and 600 °C is shown. (a) The thin film (25 °C) before scratch. (b) After scratch (25 °C)with a wafer forceps. (c) The thin film (600 °C) before scratch. (d) After scratch (600 °C) with a wafer forceps.

The result can be divided to three main categories. First, initial stage then second stage is formation stage and lastly matures stage. The sample of 25 C and 300 C can be listed under the first stage due to their low in resultant response to the N2 gas. While the sample 600 C and 700 C has achieved their mature stage by showing increase in density of dots number. The sample of 500 C will be known as second stage where some area showing low response while figure 2 d), shows growth of number of dots per area.

When the sample is undergoes SEM for further magnification, the result of sample for surface of every 1000X magnificent are shown in figure 3 below. From the SEM result, the evolution of the sample has nearly same result of the optical microscope where the growth of the uneven image of the sample can clearly see with the sample above 500 °C. Until this result, we can say that, the thermal has effect the surface morphology from nice mirror type of surface to uneven level of surface (above 500 °C).

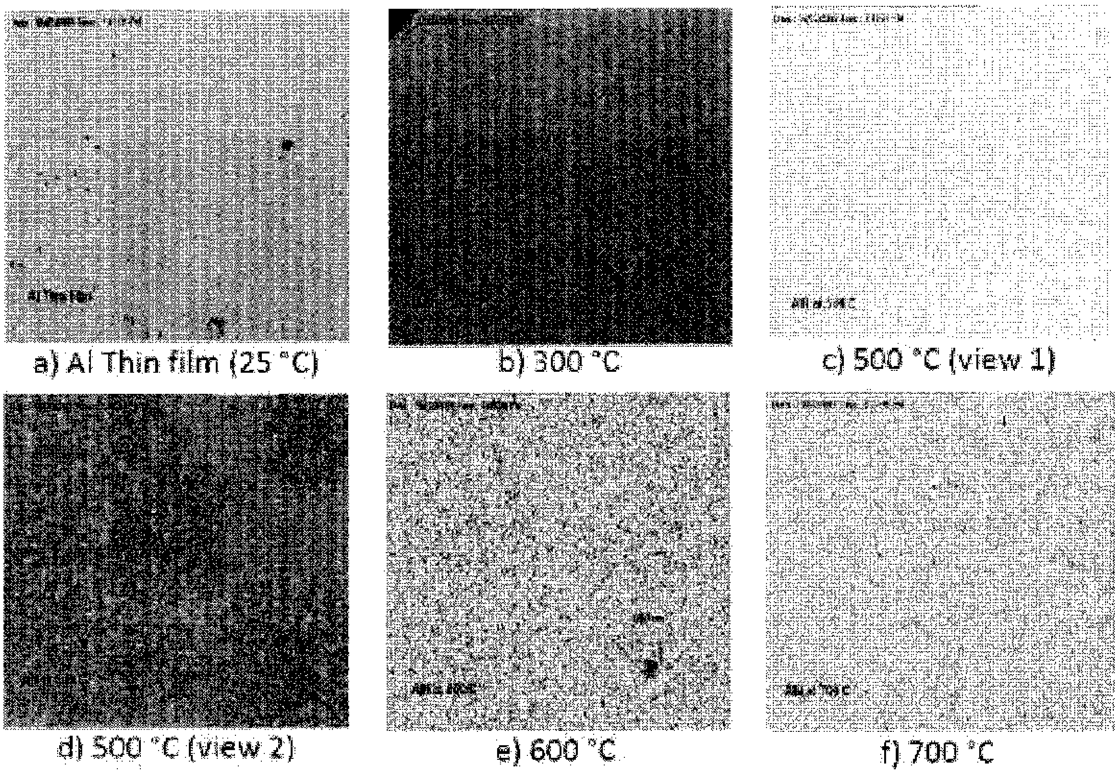


Figure 2 : The surface morphology of the thin film in the present of N2 at various temperature. a) thin film that act as control at 25 °C. b) Optical view of layer formed at temperature 300 °C. c) The dots per area increases by temperature. d) Still at 500 °C, but at different area. e) Various dots start to make shape. f) The total dots per area increases.

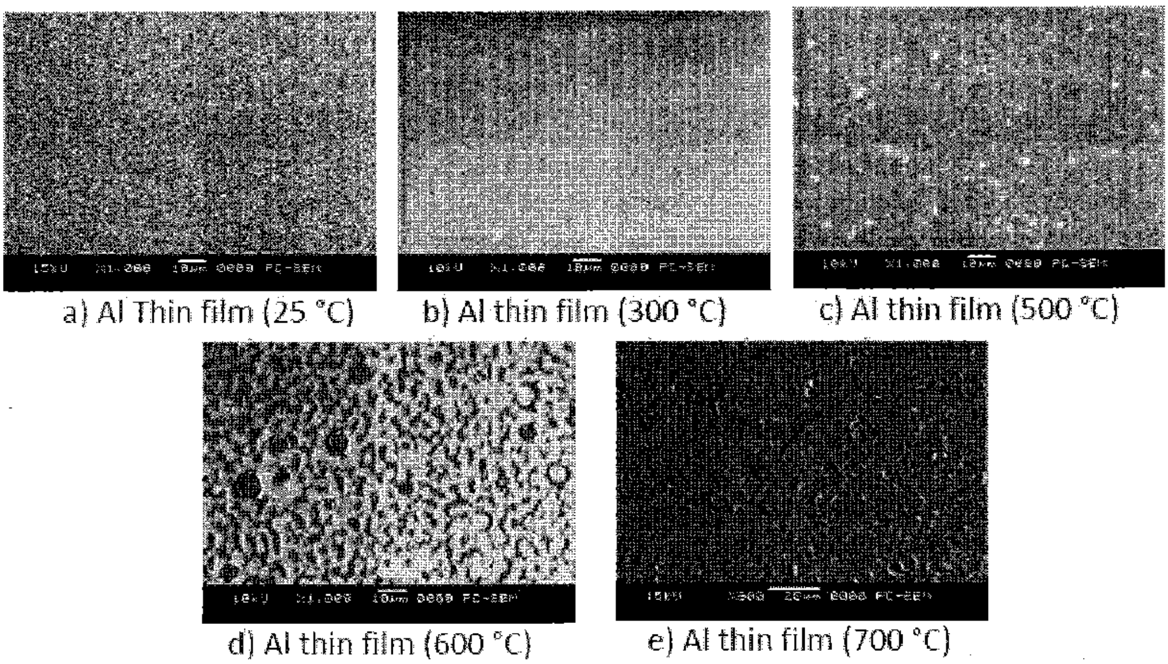


Figure 3: Surface morphology of Al thin film after the thermal process at various temperatures. The N2 flow was fixed at 10 bar.

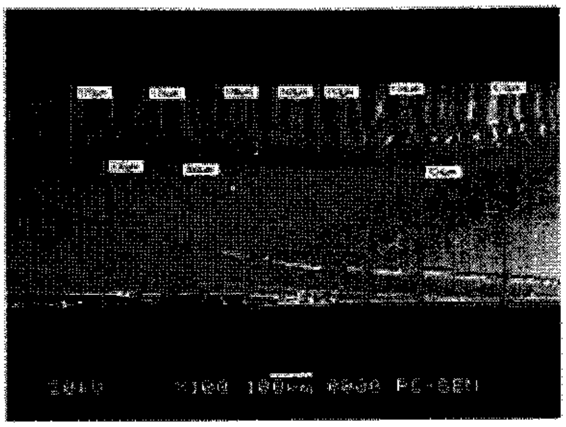


Figure 4: Cross section of substrate deposited with Al thin film. The substrate was heated at 600 °C with the present of N_2.

By using the EDS, we can determine the composition of element in a particular region. The software Analysis Station with the help of SEM unit for magnificent is used for this analysis. For example, the area labeled as 002 from the sample 600 °C are been analysis and shown in the figure 5.

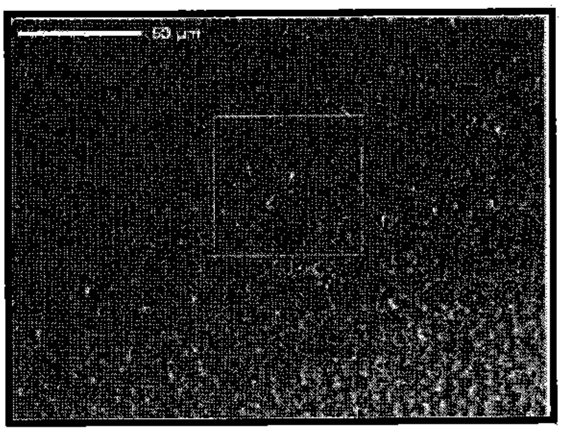
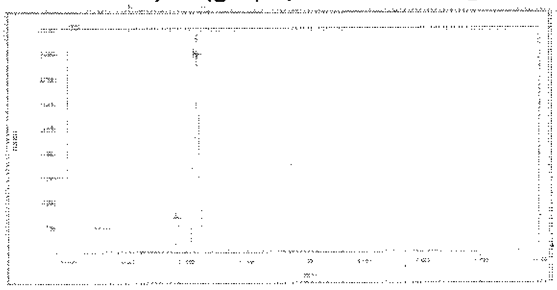
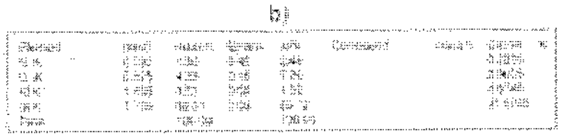


Figure 5 a): The area of 3.25 nm (label with 002) of sample 600 °C is analysis using EDS. The resultant analysis (graph) is shown in figure 4 b).



b)



c)

Figure 5 : The resultant result of sample 600 °C at area 002 is shown. b) The resultant graph with label of related element. c) The resultant element analysis in form of percentage is shown.

The test is repeated for 4 times at different area before the sample is change. The analysis of sample 600 °C is shown below with average value:-

Table 1

The resultant ratio of 5 different area on 600 °C thin film sample.

Element	Test 1	Test 2	Test 3	Test 4	Test 5	Average
Nitrogen	0	1.3	1.1	0	0	0.48
Oxygen	3.99	4.35	4.11	4.07	3.56	4.016
Aluminum	4.36	4.53	4.82	4.17	3.8	4.336
Silicon	91.65	89.81	89.97	91.22	92.64	91.058
Total	100	99.99	100	99.46	100	99.89

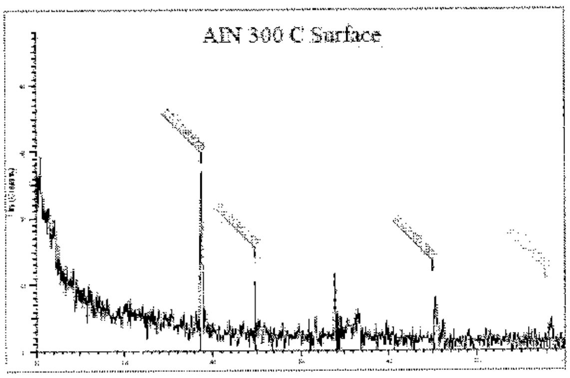
Table 2

The total resultant analysis (average value) for each sample.

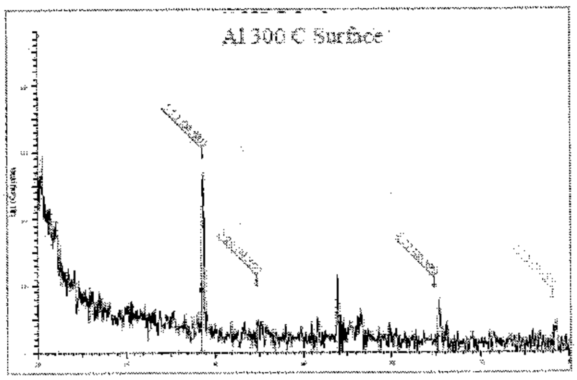
Wafer	Si (average)	AL (average)	O (average)	N (average)	Total (%)
25 C	98.764	1.236	-	-	100
300 C	93.702	6.298	-	-	100
500 C	89.66	8.318	2.022	-	100
600 C	91.058	4.336	4.016	0.48	99.89
700 C	91.53	4.408	3.918	0.146	100.002

From the table 2 above, it is known that, the elements of Oxygen (O2) only exits for sample (as shown in table) which is above than 500 °C. While the element N2 exits for sample 600 °C and 700 °C only.

Further, the samples were tested using XRD. The result of each sample is shown as below:-



a)



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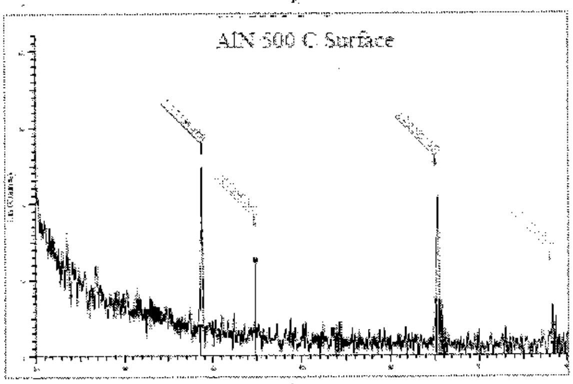

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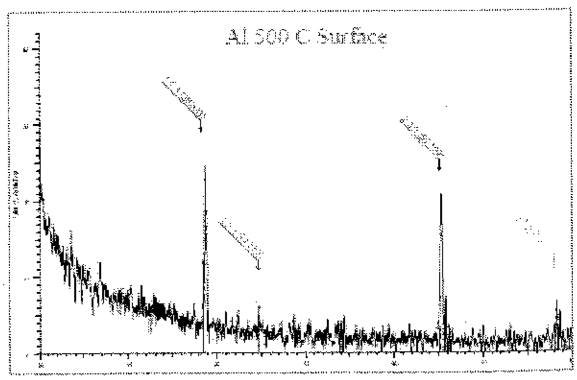

d)

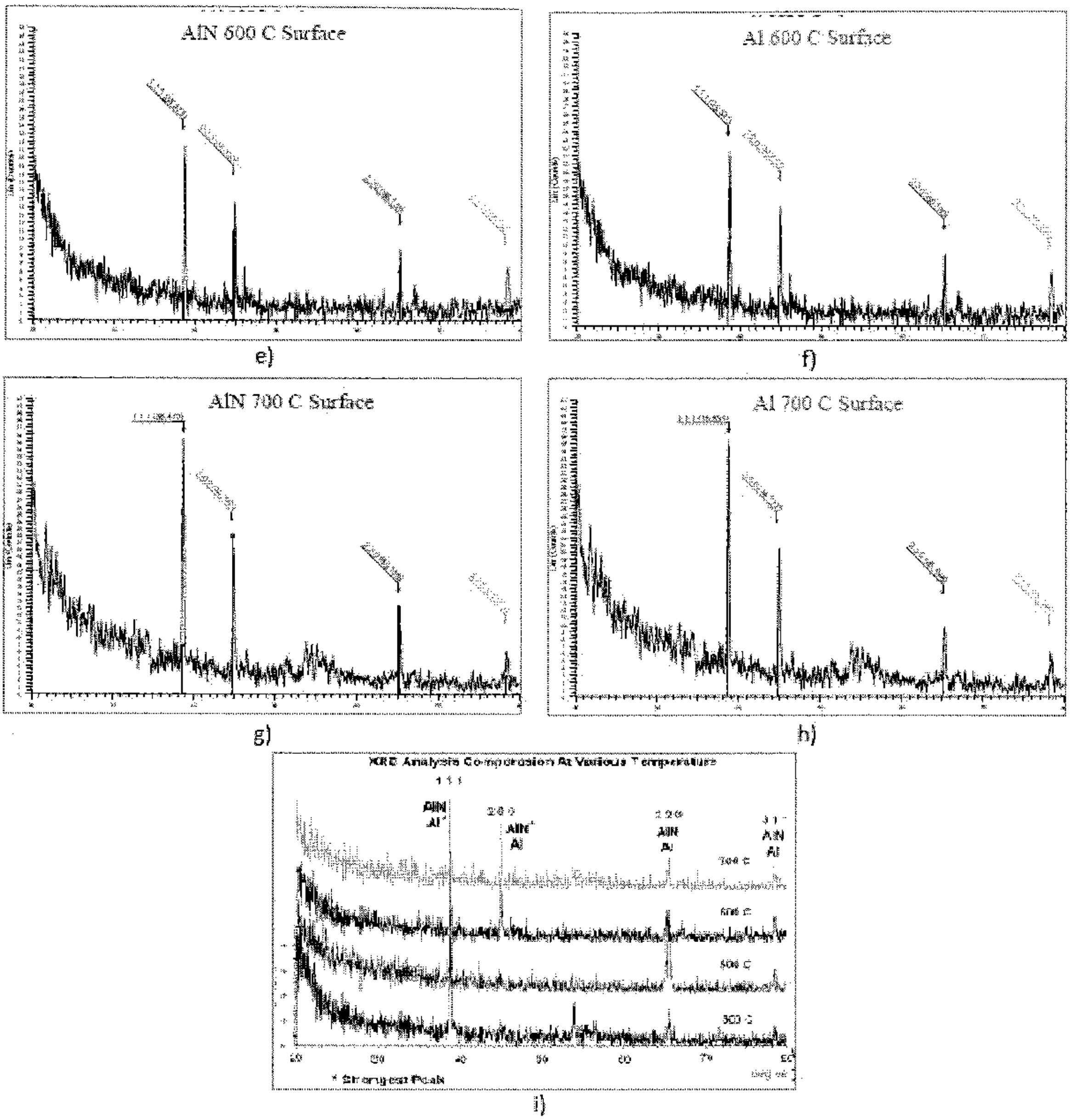

Figure 6 : The resultant result of each suspected element on the surface (theta 0.5°) sample at various temperature using XRD. a) AlN at 300 °C sample. b) Al at 300 °C sample. c) AlN at 500 °C sample. d) Al at 500 °C sample. e) AlN at 600 °C sample. f) Al at 600 °C sample. g) AlN at 700 °C sample. h) Al at 700 °C sample. i) The total comparison of 300 °C, 500 °C, 600 °C and 700 °C sample.

The figure 6 i) shows the comparison between 4 different temperature samples of 300 °C, 500 °C, 600 °C and 700 °C, which roughly show the differences that happens as the sample temperature increase. 3 major peaks (face center cubic with HKL orientation of 100, 220 and 311) are exits for all samples, while orientation of 200 shows slightly difference. The sample of 300 °C and 500 °C shows low response while the sample 600 °C and 700 °C shows positive peaks.

From the data sheet of 046 – 1200 (ALN) shows that, the strongest line of ALN should be on the orientation 200. The present strong peak on 200 (degree 44.7°) shows compound ALN is suspected exits on the surface of the 600 °C and 700 °C wafer.

The sample is further to test using I – V characterization. The result of each sample is shown as below:-

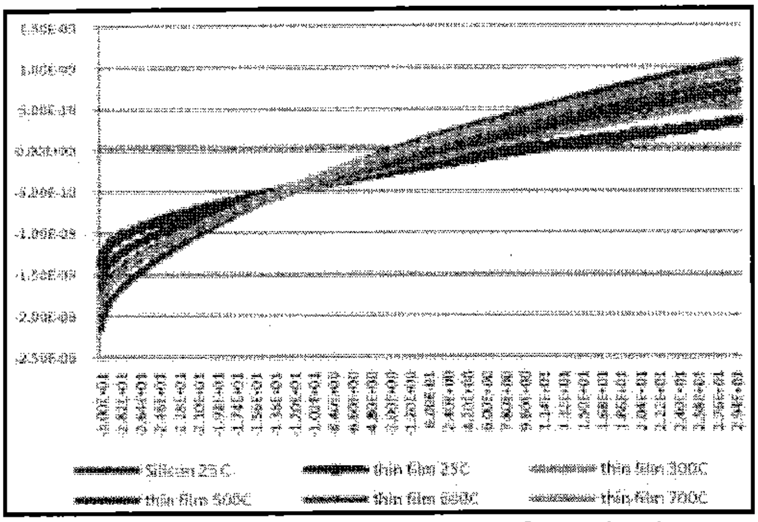

Figure 7 : The resultant result using I – V Characteristic of sample silicon 25 °C, thin film 25 °C, thin film 300 °C, thin film 500 °C, thin film 600 °C and thin film 700 °C.

The formula of sheet resistivity and bulk resistivity is shown below:-

$$\text{Sheet resistivity, } \rho = \frac{\pi}{\ln 2} \times \frac{V}{I} \qquad (1)$$

The result of each sample above is shown as below:-

Wafer	Voltage	Current	Gradient (V/ I)	Sheet resistivity O / sq
Si 25 C	29.4	$1.05e^{-9}$	$28e^{9}$	$126.9e^{9}$
AlN 25 C	29.4	$5.15e^{-10}$	$57.09e^{9}$	$258.6e^{9}$
AlN 300 C	29.4	$7e^{-10}$	$42e^{9}$	$190.4e^{9}$
AlN 500 C	29.4	$7.5e^{-10}$	$39e^{9}$	$176.8e^{9}$
AlN 600 C	29.4	$8.4e^{-10}$	$35e^{9}$	$158.6e^{9}$
AlN 700 C	29.4	$9e^{-10}$	$32.6e^{9}$	$147.6e^{9}$

From the result above, the analysis of the graph show that, the sheet resistivity of the pure Silicon wafer is 126.9e9 O/sq. When the wafer has been metalized with Aluminum metal (thin film) in the PVD, the sheet resistance has increase to a value of 258.6e9 O/sq. As the temperature increases, the value of the sheet resistance decreases from 258.6e9 O/sq (25°C) to 190.4e9 O/sq (300°C), then to 176.8e9 O/sq (500°C) before reaching 158.6e9 O/sq (600°C) and 147.6e9 O/sq (700°C). This decreasing slope from the data shows that, the rate of sheet resistivity decreases as temperature increases. From this particular test, the sample of pure Silicon wafer at 25 °C has shown the lowest sheet resistivity while the thin film 25 °C has the highest sheet resistance.

CONCLUSION

From the result obtain, it is shown that the wafer that undergoes temperature above 600 °C and 700 °C shows component of AlN exits on the surface of the wafer. This can be proven using EDS and XRD result where it shows element N is exits. The thin film also shows that, when the temperature increases, the sheet resistivity also decreases. This project has achieve 100% of the objective listed as fabricate thin film, applied thermal process and test using different equipment to understand the composition of the material.

SUGGESTION

The research on the particular method can be expand for further analysis using several other advance equipment such as Atomic Force Microscope (AFM) and Field Emission Scanning Electron Microscope (FE – SEM) to understand the phenomena happened in atomic scale . Also, it is suggested to have more samples to be tested at smaller temperature step size to understand better the reaction of thin film towards thermal effect.

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