OPTICAL AND SURFACE PROPERTIES OF AL DOPED GA_2O_3 BY ELEMENTAL STACK METHOD

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Abstract

Al doped Ga_2O_3 thin film was prepared by stacking of Al thin film on Ga_2O_3 thin film using thermal evaporator. The doping process was carried out by post annealing process at three different temperatures. The absorbance spectra revealed the Al doping process and showed low absorbance at high annealing temperature. Scanning Electron Microscope images were the evidence of surface effect due to Al diffuses at high annealing temperature (> 400°C). Energy Dispersive Spectra showed the changes in the elemental composition of Al doped Ga_2O_3 thin film for various annealing temperature and revealed Al diffusion by observed low Al content at the surface of the doped Ga_2O_3 thin film.

Keywords: *Ga_2O_3, Al doping, Optical properties, Surface analysis*

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1. INTRODUCTION

Thin-film type of semiconductor gas sensors have been developed and widely applied in various applications such as air pollution control, process control, hazard gas detection, and so forth. Gallium oxide (Ga_2O_3) is one such material, and in the last decade has been investigated for the realization of a new generation of gas sensors [1]. Ga_2O_3 is a wide band (4.8 eV) intrinsic insulator and can be changed to n-type semiconductor by doping [2].

Ga_2O_3 gas sensor is characterized as a promising high temperature sensor for the detection of reducing gases or Oxygen. At high temperature, Ga_2O_3 exhibits properties of an electronic semiconductor. The n-type semi conduction is based on an oxygen deficiency of the crystal lattice [3]. By doping these films, sensors with higher responses and lower operating temperatures may be obtained. Many researchers have already been reported the properties of doped Ga_2O_3 thin film using Co [4], Si and Sn [5, 6] and Zn as dopant. It is suitable for the next generation of optoelectronic devices operating at ultraviolet wavelength. The Si-doped Ga_2O_3 and Sn-doped Ga_2O_3 behave as the n-type semiconductor because of donor impurity and oxygen deficiency [6]. These sensors operate on the principle that the surface conduction of the sensors varies in relation to the adsorption of the ambient gas. Such changes have been noted since the earliest studies of semiconducting materials [7,8]. Various methods have been used to synthesize Ga2O3 thin film such as metal organic chemical vapor deposition (MOCVD) [9], MBE [10], floating zone [11], rf magnetron sputtering [12], photo electrochemical [13], and pulse laser ablation [9]. Thermal evaporation is a well known technique that does not produce any kind of surface damage. Because this technique is a rather gentle process it creates very little or no damage to the interface.

It is important to know the details of the surface when the element is doped into the Ga_2O_3 lattice. During the doping process, there may be a chance to affect the surface of the film depends on the dopant used. Doping process was successfully reported by several methods such as sol gel rout [14]. Stacked Elemental Layer technique was originally developed to produce $CuInSe_2$ thin films [15]. But it has also been used to produce CdTe films [16,17]. The doping process using elemental stacking is an attractive and many works has been reported and achieved good results by the same author group [18]. In this article, Al doping was performed by stacking Al elemental layer on Ga_2O_3 thin film followed by high temperature annealing process. The optical and surface properties of annealed stack are tested and reported in this paper.

2. EXPERIMENTAL WORK

Al doped Ga_2O_3 thin films were syntheszied by stacking Al thin film over Ga_2O_3 thin film using thermal evaporator (Auto evaporator). The Ga_2O_3 (99.99%) powder and Al wire (99.9%) were used as source material for this stack preperation. Initially, the vacum chamber was pumped down to $4.5x\ 10^{-5}$ mbar using the combination of rotary and diffusion pump. The source material was loaded in the boat and fixed in the elecrode inside the vaccum chamber after venting process. In the first step, Ga_2O_3 thin film was coated over Si substrate followed by Al thin film deposition. Each coating was performed at a specific time to achive desired thickness. The thickness of Ga_2O_3 and Al thin film were measured by optical method as 1.2 µm and 0.150 µm respectively. In order to achieve higher thickess, two stack configuration (Ga_2O_3/Al/Ga_2O_3/Al) was established and achieved final thickness of 2.7 µm. Secondly, to perform doping, the stack were undergon annealing process at three different temperatures of 300, 400 and 500 °C for about 2 hrs in nitrogen flow @ 6 sccm.

The optical behavior of as grown and annealed samples were tested using UV-Vis spectrophotometer. The absorbance spectra of all thin films were recorded in between 300 and 1100 nm wavelength range at 2 nm intervals. Field Emission Scannning Electron Microscopy (FESEM) was used to record and analyze the surface morphology of as grown and annealed stack. Atomic Force Microscop (AFM) was used to measure the surface roughness and grain size of Al doped Ga_2O_3 thin film before and after annealing.

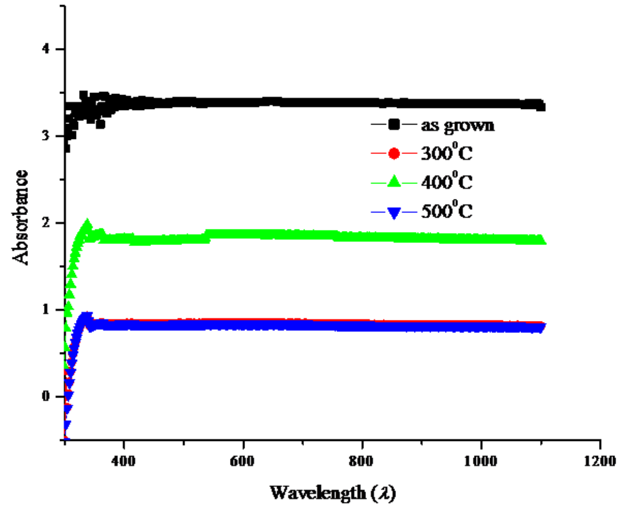

Fig1. Absorbance spectra of Al doped Ga_2O_3 thin film at different annealing temperatures.

3. RESULTS AND DISCUSSION

3.1 Optical Studies

The absorbance spectra of the non-annealed and annealed Al stacked Ga_2O_3 thin film samples at three different temperatures were recorded at the wavelength range of 300 nm to 1100 nm as shown in fig.1. A noticeable decrease in absorbance could be observed clearly for the stack annealed at 300 and 500°C. Overall, in other words, an improved transmittance can be clearly seen from the absorbance spectra for annealed samples. It depicts clearly that the annealing process helps to diffuse Al atom into the Ga_2O_3 lattice and doping occers and hence the absobance decreases. This is because of activation of Al in Ga_2O_3 by annealing process. A contrary results in absorbance could also been observed for the stack annealed at 400 °C as increased value when compared to 300 and 500 °C which could not be indentified clearly.

3.2 FESEM Analysis

FESEM characterization was carried out in order to study the surface morphology of the prepared stack before and after annealing process. The FESEM images were captured at the magnification of 100 kx and scale of 500 nm as shown in Fig. 2. Here, the SEM images revealed that the grains structure has been observed for anneald samples. Fig. 2 indicates that the annealing process induced the morphological change of the Al doped Ga_2O_3 thin film samples. From the image, it is observed that the density of the film increases as the annealing temperatures increases. The surface image of the stack annealed at 300°C shows loosly bounded particles at the surface with clear grain boundaries. The stack annealed at 400 °C shows uniform morphology with good grain growth when compared with the surface of stack annealed at other two temperatures. Surface damage with bigger particle size could be easily seen for the stack annealed at 500 °C. Overall, the annealing process influenced the surface of Al doped Ga2O3 thin film considerably. Using the surface analysis software, the particle size of doped Ga_2O_3 thin film isevaluated and the average particles size of Al doped Ga_2O_3 thin film lies in between 100 and 145 nm. Agglomorated bigger particles are absorbed with stack annealed at 500 °C.

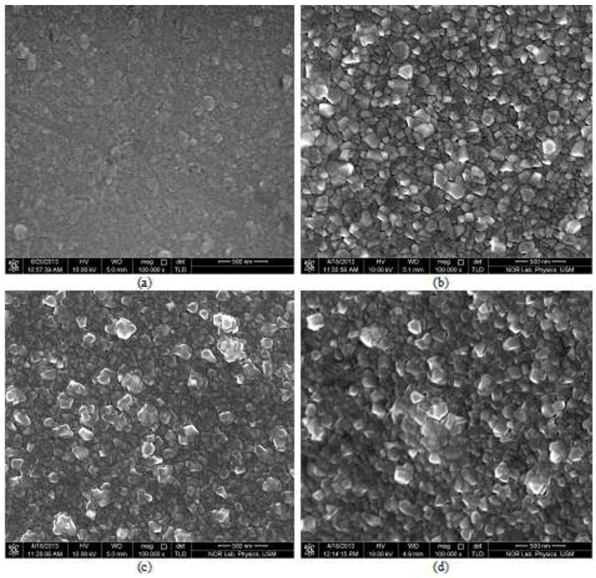

Fig2. FESEM image of the sample: (a) as-prepared, (b) annealed at 300°C, (c) annealed at 400°C and (d) annealed at 500°C.

In addition to this, the elemental composition analysis of as grown and annealed stack was also performed by recording energy dispersive spectroscopy and observed the mass percentage of elements as shown in table – 1. From table 1, the elemental mass percentage of Ga, O and Al is varying with respect to the annealing temperatures. It shows clearly that the Al content slowly decreases as the annealing temperature increases. It is attributed to the diffusion of Al into the Ga_2O_3 lattice as a result of annealing. Since Al was deposited on top of Ga_2O_3 thin film, the as grown sample has high Al mass percentage than annealed samples. It could also be observed that the gallium and oxygen content are also changed for higher annealing temperature. Especially, Ga concentration increases with 300°C and slowly decreass for the annealing temperature > 300°C. But, it does not match with the elemental composition of as grown samples.

Table1 Elemental mass percentage of Al doped Ga_2O_3 thin film stack at various annealing temperatures

Elements	As grown	300°C	400°C	500°C
O	8.8	4.72	7.24	10.40
Ga	84.1	90.10	87.61	84.98
Al	7.10	5.18	5.16	4.62

Overall, the Al and O content increases and Ga content decreases for higher annealing temperatures. In addition, it is clearly observed that the O concentration increases with annealing temperature increases.

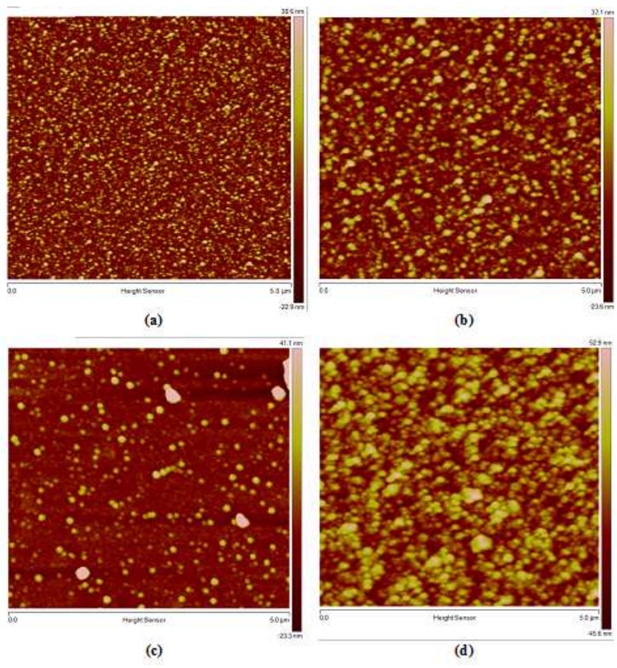

Fig3. AFM images of (a) as grown and annealed stack at (b) 300 °C, (c) 400 °C and (d) 500 °C.

3.3 AFM Analysis

To understand the surface properties in detail, the surface images of as grown and annealed Al doped Ga_2O_3 thin film were captured by AFM and presented in Fig.3. The surface image of as grown sample is shown in fig.3a. From fig.3, it is clearly understood that the Al diffusion as a result of annealing process has more influence in the surface morphology and also the particles size. Grain growth was also observed for Al doping from AFM images.

Table2 Surface parameters of Al doped Ga_2O_3 thin film measured from AFM images

	As grown	300°C	400°C	500°C
Roughness (µm)	0.0060	0.065	0.0043	0.011
Particle size (µm)	0.162	0.136	0.208	0.250

The AFM image of sample annealed at 500°C (Fig.3d) shows granular structure than other two temperatures. This may be due to grain grown as a result of high annealing temperature. It may be attributed to the high rate of diffusion of Al into Ga_2O_3 layer at high temperature which is also evidenced by EDS analysis in the previous section. Fig.3c shows smooth and dense nature when compared to the images recorded with the samples annealed at other two temperatures which is well agreed with the SEM results. For detailed analysis, the surface parameters such as roughness and particle size of the as grown and annealed samples were evaluated by analyzing the AFM images using image software and summarized in table – 2. It clealy revels that the particle size of the stack slowly increases as with annealing temperature increases from 300 °C – 500 °C. But it is also noticed that the stack annealed at 300°C has small size particles than as grown samples and increases gradually with temperatures. In roughness analysis, the surface roughness of this annealed thin film was high and showed the influence of Al diffusion on surface properties of doped Ga2O3 thin film. The improved surface roughness was noticed with the samples annealed at 300 °C and 500 °C and explained the effect of al diffusion at high temperature. In addition, very low value in surface roughness was measured with the stack annealed at 400°C. Over all, the Al diffusion into Ga_2O_3 thin film changes the surface roughness noticeably.

CONCLUSIONS

Al doped Ga_2O_3 thin film was synthesized by stacking Al layer on Ga_2O_3 thin film using themal evaporator followed by high temperature annealing process. The optical absorbance spectrum was the evidence of Al doping into Ga_2O_3 lattice with decreased absorbance for increased temperature. Surface of Ga_2O_3 thin film was modified by Al diffusion at high temperatures. Grain growth was also observed as a result of Al diffusion. Elemental composition of Al doped Ga_2O_3 thin film was showed the behavior of elemental diffusion during annealing process as O difficient. Noticeable surface roughness and particle size was achieved in post annealing process at high temperature as a result of Al diffusion.

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Shanmugan Subramani has received his bachelor degree (1997) in chemistry, diploma in (1998) chemical process instrumentation and Master degree (2000) in Energy Science. He has received his Ph.D in the field of thin film solar cells during 2009. He has published more than 65 research papers in the refereed International journals and conferences. He also has a research experience of more than 7 years. Now he is working as a Post Doctoral Research Fellow in School of Physics, University Sains Malaysia upto date. His research is focused on identifying best thermal interface material in solid state devises in semiconductor industries.

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