# SYNTHESIS GALLIUM NITRIDE THIN FILMS BY PULSED LASER DEPOSITION AS AMMONIA (NH<sub>3</sub>) GAS SENSOR

Z. E. SLAIBY, A. RAMIZY<sup>\*</sup>

University of Anbar, College of Sciences, Physics Department, Anbar, Iraq

GaN thin films were deposited on silicon substrate (Si) by pulse laser deposition in a nitrogen atmosphere to use as a gas sensor for detection Ammonia (NH<sub>3</sub>) gas. Surface morphology of gallium nitride nano thin films were characterized by atomic force microscopy (AFM). The film appears homogenous and the distribution and grain shapes is nearly uniform. High density of nanostructure GaN was created as shown in field emission scan electron microscopy (FESEM) image. XRD measurement showed that GaN have a hexagonal structure. The elemental composition of materials was identified by use of Energy Dispersive X- Ray Analysis (EDX). The average concentration of nitrogen according to EDX analysis for the samples are increase with increasing number of laser pulses. Optical measurements were performed to measure the band gap by UV-visible spectroscopy. The gas sensitivity for NH<sub>3</sub> gas were measured for fabricated gas sensor device as a function of concentration.

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## 1. Introduction

III-Nitrides semiconductors like GaN, InN and AlN, have attracted a large attention in optoelectronics devices including sensors and detectors, laser diodes (LDs) in ultraviolet and blue regions and light emitting diodes (LEDs)[1]. III-nitrides group of semiconductor materials as well revealed its excellent properties in chemical and physical inertness, mechanical and thermal stable, and thermal conductivity. It also has wurtzite crystalline structure and direct wide energy band gap [2]. The advantages related with large band gap involve high breakdown voltages, high temperature operation, it is abile to sustain big electric fields, and lower noise generation, these features make GaN which has a direct band gap of 3.4 eV, Suitable material for sensors that operate in harsh environments[3,4]. GaN thin films have been grown by different growth techniques such as molecular beam epitaxy (MBE), atomic layer epitaxy (ALE), and metal organic vapor phase expitaxy (MOVPE) which usually require high growth temperature and therefore high energy consumption [5-7]. However, good quality of GaN films were recently grown by pulsed laser deposition (PLD)[8]. In the past, this technique has been widely used to prepare high quality multicomponent oxide ceramics thin films. PLD is comparatively good growth technique and it has many advantages than other techniques like it's very simple to operate and doesn't require toxic or an expensive precursors. Growth of thin film may be achieved at relatively low substrate temperatures compared with other growth techniques [5,9]. GaN thin film can be deposit on various substrates, like Si, sapphire and glass[10-12]. The sapphire substrate is remain high cost. During this regard, this makes sapphire difficult to meet substrate requirement for growth of lowcost and high- power of GaN based devices. Si is the more abundant elements onto earth, it has good semiconducting properties and excellent thermal conductivity, thus Si substrates able to overcome problems compared with sapphire substrate in GaN-based devices preparation [7]. At present, there is a large interest in the implementation of sensing devices to improve environmental and the safety control of gases [13]. In this work, gas sensor synthesized using GaN/Si thin films which fabricated by this simple technique and sensitivity of the fabricated gas sensor for NH<sub>3</sub> gas have been studied.

<sup>\*</sup> Corresponding author: asmat\_hadithi@uoanbar.edu.iq

# 2. Experimental part

In this experiment, GaN layer was deposited on unheated n-type of Si (111) substrate by PLD technique at a pressure of  $1 \times 10^{-1}$  Torr as shown in Fig.1, to use as Ammonia (NH<sub>3</sub>) gas sensor. Si substrate was cleaned by alcohol and distilled water with ultrasonic bath, in order to remove the impurities. The targets used in PLD can be prepared by pressing GaN (purity of 99.99) in the powder form. A Nd: YAG pulsed laser in a wavelength with 1064 nm was focused on the target in repetition rate of 6 Hz. During deposition process, the energy of incident laser was preserved at 300 mJ/pulse. The annealing process was achieved at 600°C for 30 minutes. Silver (Ag) metal contact was deposited on the GaN/Si surface by vacuum evaporation system to fabricate the gas sensor. A metal mask which consisting of set of holes was used for this purpose.



Fig. 1. PLD system for thin films deposition.

# 3. Results and discussion

#### 3.1. AFM analyses

Topography of thin film prepared by pulse laser deposition studied by atomic force microscope. The film appears homogenous and the distribution and grain shapes is nearly uniform as shown in Fig. 2. The values observed of roughness and average grain size for GaN thin films are included in Table 1. It's clear that the increasing in roughness with increasing number of laser pulse. This is attributed to the increasing number of the pulses increases the thickness of this films[14], since the roughness is function of the layer thickness, roughness increases as thickness layer increases[3].

	sample	pulses Number	Sa (roughness Average)(nm)	Sq (Root Mean Square) (nm)
а	GaN/Si	300	7.4	8.55
b	GaN/Si	600	9.13	10.6
с	GaN/Si	900	14	16.1

Table 1. Root mean square (rms) and Average roughness which calculated by AFM analysis.



Fig. 2. AFM images for GaN thin film deposit on Si (a) at 300 pulses (b) at 600 pulses (c) at 900 pulses.

### **3.2. FESEM analyses**

Grain formation in GaN thin films which analyzed by FESEM. Morphology of the surface for GaN thin films is shown in Fig. 3, it can be observed that the grains are found to be with be a mixture of small and large structures, high density of nanostructured GaN was created as shown in Fig 3. From FESEM image which can be observed a cauliflower-like morphology, this result is agreement with [15], and good agreement with GaN nano thin film prepared via Plasma Enhanced-CVD by M. Gholampour et al [16].



Fig. 3. Grains observed by use FESEM analysis GaN thin film deposit on Si (a) at 300 pulses (b) at 900 pulses.

#### **3.3. XRD Analyses**

Fig. 4. showed that XRD measurement of GaN thin film grown by pulsed laser deposition on silicon substrate. The peaks in figure. 2, X- ray diffraction of GaN thin film. (a) at  $28.6273^{\circ}$  was from the silicon substrate Si (1 1 1) and the peak at  $32.639^{\circ}$ was from GaN (100), another peak at  $64.2711^{\circ}$  correspond to GaN (013), (b) at  $28.6083^{\circ}$  was from the silicon substrate Si(1 1 1) and the peak at  $58.9845^{\circ}$  was from GaN (110), therefore, our samples can be ensured to have hexagonal structure according to PDF 00-050-0792 card. Diffraction peaks subject to a small shift. This little shift may be consequent to tensile strain made by mismatch lattice between film and substrate [15].



Fig. 4. X-ray diffraction GaN thin film deposit on Si (a) at 300 pulses (b) at 900 pulses

### 3.4. EDX analyses

EDX spectrum is utilized to confirm the composition of GaN thin films deposited on Si substrate. The average concentration of nitrogen according to EDX analysis for the samples are increase with increasing number of laser pulses, where the ratio of Nitrogen atoms is 4.55% at 300 pulses of laser and 9.03% at 900 pulses of laser. From the Fig. 5 There are oxygen impurities in EDX analysis, which may be introduced from air leakage [16].



Fig. 5. EDX analyses of GaN thin film deposit on Si (a) at 300 pulses,(b) at 900 pulses.

### 3.5. Optical characterization

The transmittance spectra for GaN thin films was showed in Fig. 6. It was showed that the transmittance of GaN thin films are decrease with increasing of number of pulses, and were transparent within visible ranges. Band gap value of GaN thin film is about 3.88 eV and 3.85 eV for 300 and 900 pulses respectively as showed in Fig.7. By use the relationship between the absorption coefficient ( $\alpha$ ) and photon energy (hv) of the incident light,  $\alpha 2 \sim$ (hv-Eg), energy band gap (Eg) for GaN thin film, a little bit larger than sooner experiment results[17] which is in agreement with the findings of other research[18].



Fig. 6. Transmittance spectra of the GaN deposited film on Si



Fig. 7. The direct band gap of GaN deposited film on Si

## 3.6. Sensor measurement

For the measurements of gas sensor, the device was placed within stainless steel chamber associate with inlet and outlet for gases. To determine potential for utilization GaN as gas sensor, GaN thin films resistance was measured on a hot plate at temperatures 50 °C. Fig. 8, showed that the resistance changes over time with concentration. When the device exposure to gas, sensor resistance decreases quickly with time and then it reaches a stable value. The stable value of sensors resistance [19]. Performance also depends on the operating temperature, the decreasing of the device resistance with increasing the temperature is a common property of semiconductors [20].Fig. (9), showed that sensitivity changes with concentration of NH3 gas. The sensitivity (S) for the gases is outlined by the form:

$$\mathbf{S} = (\mathbf{R}_{\rm o} - \mathbf{R}_{\rm gas})/\mathbf{R}_{\rm o} \tag{1}$$

where  $R_o$  is that the device resistance before passing the gas and  $R_{gas}$  is the device resistance after passing it [21]. The results showed that the sensitivity of the device increased from 12.55213% to 34.0566% with concentration of the gas from 500 to 1500 (ppm) respectively. The sensors ought to be ready to follow little changes in concentration with a quick dynamic response [22].



Fig. 8. Resistance changes over time with gas. concentration



Fig. 9. Sensitivity over gas concentration

## 4. Conclusions

NH<sub>3</sub> gas sensor was prepared by used GaN thin films which grown by PLD technique on substrates of Si (111), with a N2 atmosphere in PLD chamber growth. Effect of varying the number of pulses on GaN layer morphology is observed. With increasing the number of pulses the formations of structures are varying in shape and size. From FESEM image which can be observed a cauliflower-like morphology. EDX data revealed that, with increasing pulses the presence of the nitrogen (N) element, which means that N element began to appear within the surface. Sensitivity of GaN\Si gas sensor was increase as increasing the concentration of NH<sub>3</sub> gas.

## References

- [1] Ho Xin Jing, Che Azurahanim Che Abdullah, Mohd Zaki Mohd Yusoff,
- Azzafeerah Mahyuddin, Zainuriah Hassan, Results in Physics 12, 1177 (2019).
- [2] X. W. Sun, R. F. Xiao, H. S. Kwoka, Journal of applied physics 84(10), S0021 (1998).
- [3] Asmiet Ramizy, Issam M. Ibrahim, Maryam Th. Muhammed, Optik 126, 3125 (2015).
- [4] Fong Chee Yong, Universiti Sains Malaysia 2016.
- [5] M. Baseer Haider, M. F. Al-Kuhaili, S. M. A. Durrani and Imran Bakhtiari, J. Mater. Sci. Technol. 29(8), 752e756 (2013).
- [6] R. D. Vispute, V. Talyansky, R. P. Sharma, S. Choopun, M. Downes, T. Venkatesan, K. A. Jones, A. A. Iliadis, M. Asif Khan, J. W. Yang, American Institute of Physics, S0003 (1997).
- [7] Wenliang Wang, WeijiaYang, Yunhao Lin, Shizhong Zhou, Guoqiang Li, Scientific Reports 5, 16453 (2015).
- [8] M. Cazzanelli, C. Vinegoni, D. Cole, J. G. Lunney, P. G. Middleton, C. Trager-Cowan, K. P. O'Donnell, L. Pavesi, Materials Science and Engineering B 59, 137 (1999).

- [9] B. Y. Man, C. Yang, H. Z. Zhuang, M. Liu, X. Q. Wei, H. C. Zhu, C. S. Xue, Journal of applied physics 101, 093519 (2007).
- [10] Asmiet Ramizy, Journal of Kufa Pysics 9(1), 2017.
- [11] Suatpat, Soner Ozen, Sadan Korkmaz, Journal of electronic materials 47(1), 2018.
- [12] Hasina F. Huq, Rocio Y. Garza, Roman Garcia-Perez, Journal of Modern Physics 7, 2028 (2016).
- [13] H. S. Hassan, A. B. Kashyout, I. Morsi, A. A. A. Nasser, A. Raafat, AIP Publishing LLC 978-0-7354-1295-8 (2015).
- [14] Gurpreet Kaurn, Anirban Mitra, K. L. Yadav, Natural Science Materials International 10.1016/j.pnsc.2015.01.012.
- [15] Luis Arturo Martinez-Ara, Jorge Ricardo Aguilar-Hernandez, Jorge Sastre-Hernandez, Luis Alberto Hernandez-Hernandez, Maria de los Angeles Hernandez-Perez, Patricia Maldonado-Altamirano, Rogelio Mendoza-Perez and Gerardo Contreras-Puente, Materials Research 22(2), e20180263 (2019).
- [16] M. Gholampour, A. Abdollah-zadeh, R. Poursalehi, L. Shekari, S. Hatamikhah, Procedia Materials Science 299, 30311 (2015).
- [17] R. F. Xiao, H. B. Liao, N. Cue, X. W. Sun, H. S. Kwok, 1996 American Institute of Physics S0021-8979~96!06619-4 (1996).
- [18] Asmiet Ramizy, Universiti Sains Malaysia, 2011.
- [19] P. Mitra, A.K. Mukhopadhyay, Bull. Pol. Ac.: Tech. 55(3), 2007.
- [20] Dae-Sik Lee, Jung-Hee Lee, Yong-Hyun Lee, Duk-Dong Lee, Sensors and Actuators B **6989**, 1 (2003).
- [21] Fawzy A. Mahmoud, G. Kiriakidis, Journal of Ovonic Research 5(1), 15 (2009).
- [22] Yacine Halfaya, Chris Bishop, Ali Soltani, Suresh Sundaram, Vincent Aubry, Paul L. Voss, Jean-Paul Salvestrini, Abdallah Ougazzaden, Sensors 16, 273 (2016).