

High-Quality Aligned GaN/ZnO Nanowires Grown by Thermal Evaporation for UV Detector Application

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Abstract

Gallium nitride (GaN) nanowires (NWs) were grown on Zinc oxide/silicon (ZnO/Si) (100) substrate by thermal evaporation method. The magnetron sputtering technique was used to deposit ZnO thin film. High-density nanostructured GaN was formed as shown in the scanning electron microscopy image. X-ray diffraction showed that ZnO/Si and GaN films had a hexagonal wurtzite structure. Photoluminescence (PL) of ZnO/Si showed strong peak at 382.84 nm (3.23 eV), while PL of GaN/ZnO/Si NWs exhibited a strong band-edge emission at approximately 338.94 nm (3.65 eV), which belongs to GaN NWs. Broadening of the energy bandgap compared with the growth of GaN (3.45 eV) could have occurred because of nanocrystalline structure quantum confinement effects. Raman spectrum of ZnO/Si nanocrystalline thin films showed a band located at 579 cm^{-1} that can correspond to the A₁(TO) mode. Furthermore, the Raman bands at approximately 520 cm^{-1} correspond to the first-order transverse optical (1TO) mode of the c-Si substrate. For GaN/ZnO/Si NWs, Raman-active optical phonons are assigned to 568 cm^{-1} because of E₂ (high). The I–V characteristics of GaN/ZnO/Si indicated the excellent ultraviolet photoresponse.

Key words: GaN nanowires; ZnO/Si; UV detector.

النانونواير عالي الجودة للكالسيوم نترايد/زنك اوكسايد والمحضر بطريقه التبخير الحراري
لتطبيقات كواشف الاشعه الفوق البنفسجية

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الخلاصة

تم تحضير الكالسيوم نتريد نانو واير على طبقه الزنك اوكسايد باستخدام طريقه التبخير الحراري . تم ترسيب افلام الزنك اوكسايد باستخدام طريقه التريديز . اظهرت نتائج المجهر الالكتروني تشكيل كثيف ذات تراكيب نانويه على سطح الكالسيوم نتريد . اظهرت نتائج حيود الاشعه السينيه ان ألكالسيوم نترايد/زنك اوكسايد كلاهما يمتلكان تركيب سداسي. بينت دراسه التلؤلؤيه الضوئيه للزنك اوكسايد/سليكون ظهور قمه ذات شدة عاليه عند 382.84 نانوميتر (3.23 إلكترون فولت) وكذلك اظهرت ان الكالسيوم نتريد/ للزنك اوكسايد/سليكون يمتلك حافه حزمه انبعاث حاده عند 338.94 نانوميتر

(٣.٦٥ إلكترون فولت) والتي تعود للتركيب الكاليوم نتريد نانو واير. أظهرت النتائج ان هناك تعريض في فجوة الطاقة البصريه لكاليوم نتريد ذات التركيب النانوييه مقارنة بالتركيب الحجمي الاعتيادي والذي يعود سببه الى تأثير الحصر الكمي عند الابعاد النانويه. ايضا بينت نتائج فحص رامان ظهور انماط اهتزازيه عند ٥٦٨, ٥٢٠, ٥٧٩ سم⁻¹ تابعه لى للزنك او كسايد/سليكون بنمط (A1(TO)) ولسليكون بنمط (1TO) والكاليوم نتريد/ للزنك او كسايد/سليكون بنمط (E2(High)). اشارت دراسه الخصائص الكهربائيه ان الفلم المحضر بيدي استجابيه جيده كمتحسس للاشعه فوق البنفسجيه.

كلمات مفتاحية: الكاليوم نتريد نانو واير؛ ZnO/Si؛ كواشف الاشعه فوق البنفسجيه.

1. Introduction

Nanostructure materials have recently been the focus of an extensive interest because of their potential applications in microelectronics and optoelectronics field. The wide-bandgap semiconductor gallium nitride (GaN) is a promising material and plays an important role in the fabrication of optoelectronic devices, such as detectors and sensors, because of its large direct energy bandgap of 3.45 eV at room temperature [1, 2]. GaN thin films can be grown on different substrates, such as sapphire or c-Si. If silicon (Si) substrate is used for GaN films growth, then large GaN substrates can be produced from cheap Si wafers. More importantly, Si-based electronic devices can be easily integrated. However, GaN films cannot be easily grown on Si substrate because of large lattice mismatch (17%) and large thermal expansion coefficient difference (56%) between Si and GaN. Therefore, using a suitable buffer layer, such as zinc oxide (ZnO), to accommodate these mismatches is necessary [3, 4]. The growth of GaN film on ZnO film is important because of the similar material properties of GaN (III–V type) and ZnO (II–VI type). ZnO has a hexagonal wurtzite structure with lattice constants close to those of GaN (very small lattice mismatch of orientation, with a of approximately 1.9% and c of approximately 0.4%) and nearly similar thermal expansion coefficients to those of GaN [5, 6].

The large energy bandgap of GaN (approximately 3.45 eV) and ZnO (approximately 3.37 eV) enable the use of GaN and ZnO in light-emitting devices in the blue, violet, and ultraviolet (UV) spectral regions (GaN and ZnO) are unresponsive to infrared radiation because of the cut-off course in long wavelength) [7, 8]. UV photodetector is one of these devices and has many kinds, such as "flame, ozone and water purification detection" [9, 10].

This study aimed to prepare GaN/ZnO nanowires (NWs) using the thermal evaporation technique, which can be considered as a novel fabrication procedure for GaN semiconductor heterostructure.

2. Experimental Part

In this work, thin films of the ZnO material were deposited onto the n-type of Si (100) substrate. An Edwards Auto 500 Radio Frequency (RF) Sputtering System equipped with a QC Scientific Precision Chiller was employed to sputter ZnO layers onto Si (100).

A well-known cleaning technique, namely the Radio Corporation of America technique, was used prior to the sputtering process to clean native oxide layer. This is done by placing the substrate in the sputtering chamber about 10 cm from the ZnO. This process lasted for 10 min. The purity of the ZnO was around 99.9% with 3.5 cm in length, and 0.25 in thickness. The

first step in the deposition, as shown in (Figure 1), started by evacuating the sputtering chamber down to pressure of 5×10^{-5} mbar. In the next step, the Argon gas was pumped into the system until the pressure reached 2.3×10^{-2} mbar.

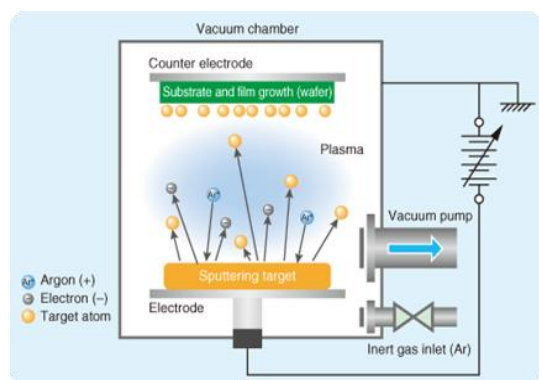


Figure 1: Schematic diagram of the sputtering technique.

The sputtering operation was done with RF power of 200 W, which lasted for 120 min to let the ZnO layer deposit with estimated thickness of 1.1 μm [11]. The GaN NWs were prepared by thermal evaporation method using GaN powder with 99.999% purity at 1,000 °C for 120 min under the Argon gas pump 0.5 cm^3/min . Subsequently, GaN powder was deposited onto ZnO film by thermal evaporation without using catalyst used during synthesis. Platinum (Pt) metal contact with a thickness of 200 nm was deposited onto the surface of GaN/ZnO/Si using the RF sputtering system to fabricate the photosensor. A metal mask consisting of an array of holes with a diameter of approximately 0.9 mm was used for this purpose. Pt was used for Schottky contact because of its high work function value.

Surface morphology and structural properties of nanostructures were analyzed using scanning electron microscopy (SEM), and X-ray diffraction (XRD). Photoluminescence (PL) measurement was also performed at room temperature using

an He–Cd laser ($\lambda=325$ nm) and Raman scattering has been investigated using an Ar^+ Laser ($\lambda=514$ nm)).

3. Results and Discussion

3.1. Morphological Properties

The morphological properties of the ZnO/Si and GaN/ZnO/Si samples were examined by SEM. Figure 2a shows the SEM image of the highly dense and growth of ZnO nanostructures on Si (100) substrate. Flower-shaped of ZnO nanostructures appeared to cover the entire area of the Si substrate. Figure 2b shows the SEM image of GaN grown on ZnO as layer and deposited onto Si substrate. NWs were formed, and thin film was grown with a high density. GaN was formed and shaped as a highly dense and well-aligned NW nanostructure, which may be due to the high temperature and gas flow through the tube.

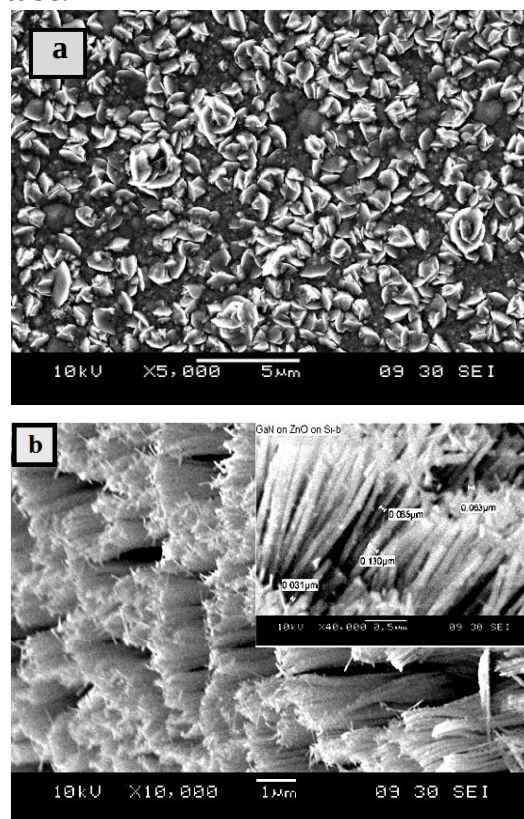


Figure 2: SEM images of of as deposit ZnO/Si nanocrystalline thin film and GaN/ZnO/Si NWs.

3.2. Structural Properties

Structural properties of the prepared samples were characterized by XRD. Figure 3 (black line) shows the diffraction peaks that correspond to the (002) and (101) planes of ZnO structure were located at 34.225° and 36.225° , respectively. The hexagonal wurtzite structure of ZnO exhibited a strong peak along the (002) orientation. The high-intensity diffraction peak at $2\theta = 69.5^\circ$ corresponds to the (100) orientation of Si substrate. Figure 3 (red line) shows the high-intensity diffraction peaks of GaN NWs grown on ZnO/Si substrate at 34.54° and 44.56° owing to GaN (0002) and GaN (321), respectively. These peaks indicate the (0002) and (321) orientations of the film. Other peaks of the GaN NWs were observed at 36.02° , 58.3° , and 64.8° corresponding to the (101), (110), and (103) orientations, respectively. The sharp peaks could be refer to a hexagonal wurtzite structure of GaN with lattice constants " $a = 3,187 \text{ \AA}$ and $c = 5,185 \text{ \AA}$ ", which are close to bulk GaN crystals reported values [12]. The sharp diffraction peaks reveal that the synthesized GaN NWs with high crystallinity [13], which may be due to effect of the large area to the small volume of ZnO nanostructure onto GaN thin film which was grown on its.

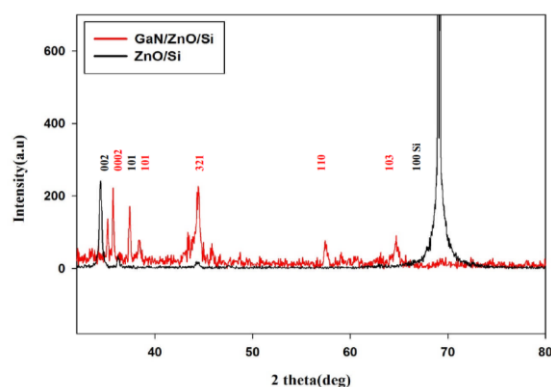


Figure 3: X-ray diffraction pattern of: of as deposit ZnO/Si nanocrystalline thin film and GaN/ZnO/Si NWs .

3.3. Optical Properties

Figure 4 shows the PL spectra of ZnO/Si and GaN/ZnO/Si NWs. The PL spectra of ZnO/Si showed three emission peaks. The strong band-edge emission high-intensity UV peak at approximately 344 nm (3.23 eV) corresponds to exciton emission from "near the conduction band to the valence band" transition. The PL peak is close to the optical bandgap of bulk ZnO [14]. Moreover, the high-intensity of UV emission peak of ZnO/Si can be related to the high crystallinity of ZnO thin films prepared by RF sputtering. Two weak defect emission bands located at 509 nm and 760 nm were also observed. The green emission band that located at 509 nm (2.43 eV) may be derived from Zn interstitials donor level electronic transition to the acceptor energy level of Zn vacancies. The electronic transition between the anti-oxygen (OZn) and conduction bands leads to the peak located at 760 nm (1.63 eV) [15-17]. The PL spectra of the GaN/ZnO/Si NWs showed that the strong band-edge emission peak at approximately 338.94 nm (3.65 eV) belongs to GaN NWs. In GaN, the band-edge emission is known to originate from donor-acceptor pair recombination and the associated phonon replicas. The increase in intensity of the donor-acceptor pair luminescence was attributed to the increase in the number of vacancy-related donors. The broadening of the energy bandgap compared with the grown GaN (3.45 eV) [18] could have occurred because of the "quantum confinement effects" of the nanocrystalline structure [19] or could be attributed to the radiative recombination of the thermalized electrons and holes. In this case, the charge carriers are in quasi-equilibrium. The shift in the peak position of GaN NWs is related

to the relaxation of hot charge carriers that formed during band bending [20].

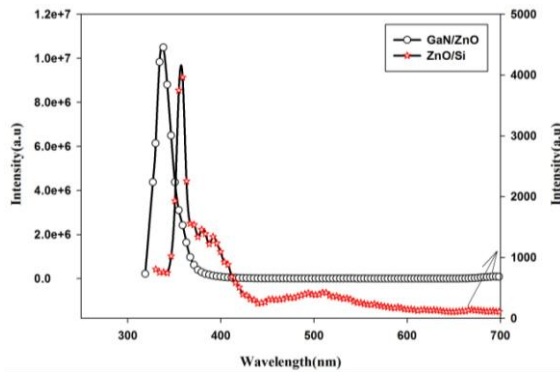


Figure 4: PL spectra of of as deposit ZnO/Si nanocrystalline thin film and GaN/ZnO/Si NWs.

Figure 5 shows the Raman shift of the ZnO/Si nanocrystalline thin film and GaN/ZnO/Si sample. The very small band at 376 cm^{-1} of the ZnO/Si sample may be related to the Raman-active zone-center optical phonons (A1) of the transverse optical (TO) mode [20]. The ZnO/Si sample showed a weak Raman band located at a wave number of approximately 437 cm^{-1} , which can be related to $E_2^{(2)}$ (high) of Raman-active modes [21]. However, the location of $E_2^{(2)}$ (high) of ZnO nanostructures can be shifted because of many reasons, such as the structure shape, impurity type, and vacancies concentration [22, 23]. ZnO/Si nanocrystalline thin films also showed a band peaking at 579 cm^{-1} that can correspond to the A1(TO) mode. Furthermore, the Raman bands at approximately 520 cm^{-1} correspond to the first-order transverse optical (1TO) mode and to the c-Si substrate [24]. For GaN/ZnO/Si NWs, Raman-active optical phonons are assigned to 568 cm^{-1} because of E_2 (high) and at approximately 520 cm^{-1} correspond to the 1TO mode and to the c-Si substrate [25].

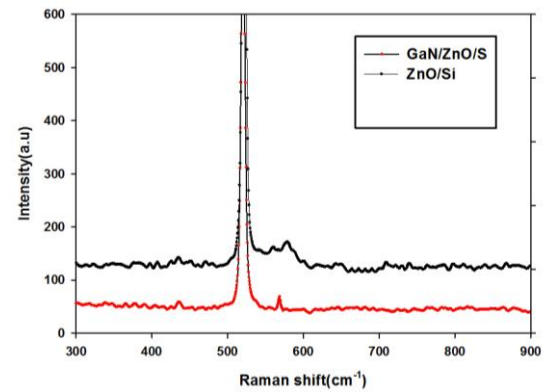


Figure 5: Raman shift of as deposit ZnO/Si nanocrystalline thin film and GaN/ZnO/Si NWs.

3.4. Current–Voltage (I – V) Characteristics

The current–voltage characteristics of GaN/ZnO/Si NW photosensor have been measured at room temperature in conditions of dark , light, and UV light illuminations under 365 nm and intensity 10mW at forward and reverse biases of I – V (-5 V to 5 V). The I – V characteristics in dark and light conditions did not exhibit any significant difference but showed an exponential behavior with a weak current. Upon illumination with UV light, sharp increments in the current were observed, as shown in Figure 6.

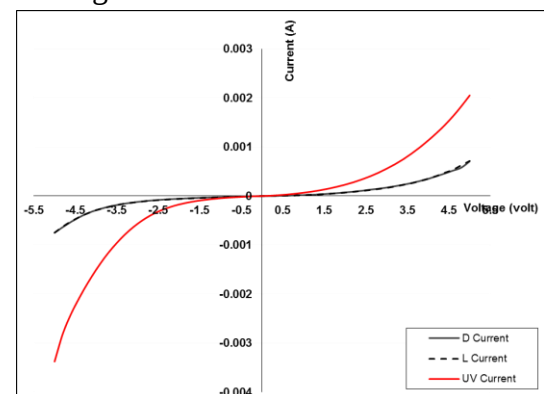


Figure 6: I – V characteristics for GaN/ZnO/Si heterojunction at forward and reverse bias voltage under dark, light source, and UV light.

A significant enhancement was observed when the device was illuminated

by UV light. When the sample was exposed to UV light, the GaN NWs absorb UV light and create enormous amount of photoexcited electron-hole pairs inside GaN layer as a result of photon energy of the incident light is higher than the bandgap of GaN [26, 27]. These electrons and holes in the depletion region of the ZnO/GaN structure streamed in the opposite directions in the presence of the electric field in the depletion region of GaN film under reverse bias operation, resulting to collect of excess photocurrent and contributing to the increase in the external current. The characteristics of nanocrystal materials with high surface-to-volume ratio appear in GaN nanostructures and the deep-level surface trap states produce a long photocarrier lifetime. The short transit time and long lifetime of charge carriers are responsible for the high sensitivity of fabricated NW photosensor under UV illumination. This behavior of the GaN NW Photosensor indicated that the film can, in somehow, recognize the UV light. In the reverse bias operation, a clear rectifying behavior can be observed as a result of creation more free electron-hole pairs. Moreover, the amount of photo-current is enhanced with the increasing of the applied reverse-biased and this is due to improvement of the carrier

collection [10, 25]. Typically, the resistance will be reduced, when the junction is exposed to a light with suitable frequency, as a direct result of creating more electron-hole pairs [28,29].

4. Conclusion

SEM images showed a highly dense GaN NW growth on high-quality ZnO film with flower-shaped nanoparticles. XRD showed that ZnO/Si and GaN films had a hexagonal wurtzite structure. The sharp X-ray diffraction peaks reveal that the synthesized GaN NWs with high crystallinity. The broadening of the energy bandgap compared with the as grown of GaN (3.45 eV) could be occurred as a results of quantum confinement effects of the NWs structures or due to the radiative recombination of the thermalized electrons and holes during the thermal processing. For GaN/ZnO/Si NWs, Raman-active optical phonons are defined by 568 cm^{-1} because of E_2 (high) and at approximately 520 cm^{-1} correspond to the 1TO mode and to the c-Si substrate. For GaN/ZnO/Si NWs, Raman-active optical phonons are assigned to 568 cm^{-1} because of E_2 (high). The $I-V$ characteristics of GaN/ZnO/Si NWs indicated a good sensitivity to UV light.

References

- [1] Magnetron Sputtering," Chinese Journal of Physics, Vol. 46, NO. 2, pp. 163-169, (2008).
- [2] Ludwig Ostlund, Qin Wang, Romain Esteve, Susanne Almqvist, David Rihntesberg, Sergey Reshanov, Andy Z. Z. Zhang, Jang-Kwon Lim, Mietek Bakowski, Adolf Schoner, Wlodek Kaplan, "4H- and 6H-SiC UV photodetectors," Physica Status Solidi C, Vol. 9, No. 7, pp. 1680-1682, (2012).
- [3] C. Yang, B. Man, H. Zhuang, X. Wei, M. Liu, and Ch. Xue, "Annealing of GaN/ZnO/Si Films Deposited by Pulsed Laser Deposition," Japanese Journal of Applied Physics, Vol. 46, No. 2, pp. 526–529, (2007).
- [4] J.W. Lee, S.W. Park, and J.B. Yoo, "The Application of a Low Temperature GaN Buffer Layer to Thick GaN Film Growth on ZnO/Si

- Substrate," *Physica Status Solidi (a)*, Vol. 176, No. 14, pp. 583-588, (1999).
- [5] S. Jin An, W. II Park, G.-C. Yi, Y.-J. Kim, H.-B. Kang, and M. Kim, "Heteroepitaxial Fabrication and Structural Characterizations of Ultrafine GaN/ZnO Coaxial Nanorod Heterostructures," *Applied Physics Letters*, Vol. 84, No. 18, pp. 3612–3614, (2004).
- [6] B. Y. Man, C. Yang, H. Z. Zhuang, M. Liu, X. Q. WEI, H. C. Zhu, and C. S. Xue, "Effects of ZnO Buffer Layers on the Fabrication of GaN Films Using Pulsed Laser Deposition," *Journal of Applied Physics*, Vol. 101, Issue 9, P-5, (2007).
- [7] H. Binti Abdul Hamid, "Fabrication, Structural and Electrical Characteristics of Zinc Oxide (ZnO) Thin Films by Direct Current Sputtering Haslinda," *Universiti Sains, Malaysia*, (2009).
- [8] N. N. Jandow, et al, "Characteristics of ZnO MSM UV Photodetector with Ni Contact Electrodes on Polypropylene Carbonate (PPC) Plastic Substrate," *Current Applied Physics*, Vol. 10, No. 6, pp. 1452- 1455, (2010).
- [9] S.J. Young, L.W. Ji, S.J. Chang, S.H. Liang, K.T. Lam, T.H. Fang, K.J. Chen, X.L. Du, Q.K. Xue, "ZnO-based MIS Photodetectors," *Sensors and Actuators A*, Vol. 135, No. 2, pp. 529-533, (2007).
- [10] P. Hazra, S. K. Singh, and S. Jit, "Ultraviolet Photodetection Properties of ZnO/Si Heterojunction Diodes Fabricated by ALD Technique without Using a Buffer Layer," *Journal of semiconductor Technology and Science*, Vol.14, No.1, pp. 117-123, (2014).
- [11] M. A. Mahdi, A. Ramizy, H.F. Al-taay, "Preparation and characterization of Porous ZnO Nanostructures Grown onto Silicon Substrate" *Journal of Ovonic Research*, Vol. 13, No. 3, , p. 135 – 141. (2017)
- [12] P. Perlin, C. Jauberthie-Carillon, J.P. Itie, A. San Miguel, I. Grzegory, A. Polian, Raman scattering and X-ray-absorption spectroscopy in gallium nitride under high pressure, *Phys. Rev. B* 45 (1) 83, (1992).
- [13] J. Wang, D. Yu, C. Li, J. Zhou, Y. Wang, S. Feng, Large-scale synthesis of single phase, high-quality GaN nanocrystallites, *Appl. Phys. A: Mater. Sci. Process.* 78 (5) 753–755, (2004).
- [14] Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, A comprehensive review of ZnO materials and devices, *Journal of Applied Physics*, 98 041301-041404, (2005).
- [15] X. Wei, R. Zhao, M. Shao, X. Xu and J. Huang, "Fabrication and Properties of ZnO/GaN Heterostructure Nanocolumnar Thin Film on Si (111) substrate," *Wei et al. Nanoscale Research Letters*, Vol. 112, No. 8, P-7, (2013).
- [16] B. Lin and Z. Fu, Y. Jia, "Green Luminescent Center in Undoped Zinc Oxide Films Deposited on Silicon Substrates," *Applied Physics Letters*, Vol. 79, No. 7, pp. 943-945, (2001).
- [17] A. Janotti, C.G. Van de Walle, Fundamentals of zinc oxide as a semiconductor by Reports on Progress in Physics, 72 126501-126530, (2009).
- [18] H.W. Kim, S.H. Shim and C. Lee, "Annealing Effects on GaN/ZnO/Si Structures Prepared by RF Magnetron Sputtering," *Materials Science Forum*, Vol. 518, pp. 137-142, (2006).
- [19] A. Ramizy, Z. Hassan, K. Omar, Porous GaN on Si (1 1 1) and its application to hydrogen gas sensor, *Sens. Actuators B: Chem.* 155 699–708, (2011).

- [20] L. Shekari *, A. Ramizy, K. Omar, H. Abu Hassan, Z. Hassan High-quality GaN nanowires grown on Si and porous silicon by thermal evaporation, *Applied Surface Science* 263 50–53, (2012)
- [21] B. Hadzic, N. Romcevic, M. Romcevic, I. Kuryliszyn-Kudelska, W. Dobrowolski, U. Narkiewicz, D. Sibera, Raman study of surface optical phonons in hydrothermally obtained ZnO(Mn) nanoparticles, *Optical Materials*, 58 317-322. (2016).
- [22] J. Kong, D. Fan, Y. Zhu, Synthesis and Raman spectra of hammer-shaped ZnO nanostructures via thermal evaporation growth, *Materials Science in Semiconductor Processing* 15 258–263, (2012).
- [23] D. Shuanga, B. Wangb, X.L. Zhongb, H.L. Yanb, Raman scattering and cathodoluminescence properties of flower-like manganese doped ZnO nanorods, *Materials Science in Semiconductor Processing* 10 97-102, (2007).
- [24] H.F. Al-Taay, M.A. Mahdi, D. Parlevliet, Z. Hassan, P. Jennings, Preparation and characterization of silicon nanowires catalyzed by aluminum, *Physica E*, 48 21-28, (2013).
- [25] Asmiet Ramizy, Khalid Omar , Z. Hassan ,Omar Alattas. The effect of sub-band gap photon illumination on the properties of GaN layers grown on Si(111) by MBE, *J Nanopart Res* 13:7139–7148, (2011).
- [26] L. Luo, Y.F. Zhang, S. S. Mao, L.W. Lin, "Fabrication and Characterization of ZnO Nanowires Based UV Photodiodes," *Sensors and Actuators A*, 127, pp. 201-206, (2006).
- [27] C. Soci, A. Zhang, X.Y. Bao, H.K. Kim, Y. Lo, D. Wang, "Nanowire photodetectors," *Journal of Nanoscience and Nanotechnology*, Vol. 10, pp. 1-20, (2010).
- [28] L.S. Chuah and Z. Hassan "GaN-based Photodiodes on Silicon Substrates, *Advances in Photodiodes*," Prof. Gian Franco Dalla Betta (Ed.), ISBN: 978-953-307-163-3, InTech, pp.331-348, (2011).
- [29] J. H. He, S. T. Ho, T. B. Wu, L.J. Chen, Z. L. Wang, "Electrical and Photoelectrical Performances of Nano-Photodiode Based on ZnO Nanowires," *Chemical Physics Letters*, vol. 435, pp. 119-122, (2007).