

Physical Properties of Nb₂O₅ Thin Films Prepared at 12M Ammonium Concentration

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Abstract. The Nb₂O₅ films were successfully prepared on the quartz substrates using chemical method. Ammonium was used as a main raw material with niobic acid solution at 12 M concentration. The XRD results ensure the formation of the monoclinic crystalline structure of the niobium pentoxide. A wide optical band gap was obtained and found to be about 3.33 eV. Clear absorption in the UV region verifies wide range of the spectrum wavelength. The surface roughness measurement indicates a good uniformity and crack-free surface. The films exhibit almost constant optical conductivity irrespective of wavelength tunability.

INTRODUCTION

In the bygone decenniums, extended potentials have been made to improve different kinds of nanostructure in establishing nanodevices like photodetectors [1, 2] field-effect transistors (FETs) [3, 4], light emission diodes (LEDs) [5, 6], and others. In specific, one of the generalities significant semiconductor devices, photodetectors that transform optical signals to electrical ones possess broad implementations in binary switches, imaging, remembrance storage, light communication, and optoelectronic loops [7-9]. Nb₂O₅ is a novel material which has established many substantial implementation in the domain of optical waveguides [10], antireflective or antireflection (AR) coatings, interference filters [11-13], catalysis [14], electroluminescent and electrochromism devices [15], gas sensing [16], biocompatible prostheses [17], batteries[18] and dye sensitized solar cells (DSSCs) [19-21].

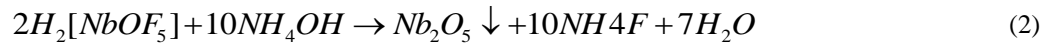
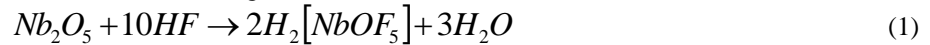
The pure niobia has an excessively complicated crystalline morphologic attitude, the confirming niobium oxide as well as displays polymorphic with thermal treatment. In universal, pure Nb₂O₅ possesses the structure of an octahedrally coordinated NbO₆ in which deformations rely on how the polyhedrons are participated [22-24]. In addition, the niobium-oxygen arrangement is complex and has narrow perversions in Nb₂O₅ stoichiometry. Therefore, highly influences the material physical attributes. For example, a little oxygen reduction leads up to the transformation from insulating to n-type semiconducting conduit [19, 25-28].

Nb₂O₅ is one of the helpful optical thin film materials on account of its desired characteristics, inclusive an excellent chemical stabilization in air and water, corrosion impedance in both acidic and alkaline media and displays band levels close to water redox potentials. The Nb₂O₅ thin films have the characteristics of rise refractive index, depressed extinction coefficient, and rise transparent proportion in the UV-vis-NIR (ultraviolet-visible near-infrared) region [29, 30]. Furthermore, the Nb₂O₅ thin films properties are exceedingly depended on the sputtered materials, precipitation mechanisms, parameters of deposition, and its thicknesses [12]. Various procedures can be used to precipitate Nb₂O₅ thin films such as spin coating, thermal oxidation, magnetron sputtering, sol-gel methods, and chemical vapor deposition [31-34].

This work presents the preparation of Nb₂O₅ thin films on quartz substrate using niobic acid solution with ammonium at a specific concentration of 12M. Surface morphology, structural and optical properties were investigated and analysed.

EXPERIMENTAL WORK

Niobium pentoxide powder (0.2 g) with ultra purity (99.99%) was used to prepare the Nb₂O₅ colloidal solution. Firstly, the powder was dissolved in hydrofluoric acid (HF) in water path at 100 °C and continuously stirred for 1 hour until the solution became totally transparency, giving an indication for total salvation of Nb₂O₅ powder according to equation (1). Next, DIW and ethanol were added to dilute the solution, and then ammonium hydroxide NH₃OH in 12 mol/l concentration was added to produce the niobium pentoxide colloidal solution according to equation (2). The molar ratios for the added chemicals are 4, 1, and 1 for HF, DIW, and ethanol respectively. All the above mentioned chemical reactions take the following chemical formulas [3]:



The thin films were prepared using the layer by layer spin coating growth at 1500 rpm for 1 min. The film was dried in drying oven with 100 °C for 15 min on quartz, p-type and n-type silicon substrates. This process was repeated three times to producing three layers of films whereby the thickness of each layer was measured to be 150 nm as observed on a scanning optical reflectometer (Fill metrics F20, USA). Heat-treated at 600 °C using a burning furnace was also done. The structural properties of the prepared films were investigated by using x-ray diffractometer (Shimadzu 6000), the grain size D , density of dislocation δ , and strain ε were extracted using the following equations [30, 35-37]:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (3)$$

$$\delta = \frac{1}{D^2} \quad (4)$$

$$\varepsilon = \frac{\beta}{4 \tan \theta} \quad (5)$$

where D is the grain size in nm, β is the peak full width at half maximum in rad, θ is the Braggs angle in deg. The optical properties were investigated by employing T60 UV-Vis spectrophotometer in the range of 200-900 nm. The energy band gap, E_g of the intended thin films was determined by extrapolating the linear part of the plot between $(\alpha h\nu)^2$ and the incident photon energy ($h\nu$) according to the following equation [38-40]:

$$(\alpha h\nu) = B(h\nu - E_g)^{1/2} \quad (6)$$

where B is a constant and α is the absorption coefficient which dependent on the thickness (t) and the transmitting ($Trans$) [41]

$$\alpha = \frac{1}{t} \ln \frac{1}{Trans} \quad (7)$$

Extinction coefficient, K and optical conductivity, σ are also measured using the following relations [42-45] :

$$K = \frac{\alpha\lambda}{4\pi} \quad (8)$$

$$\sigma = \frac{\alpha n}{4} \quad (9)$$

Using SPM and atomic force microscope AFM the morphological properties were acquired.

RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the thin films. The diffraction peaks were located at 14.20, 17.20, 18.80 and 25.50 and corresponding to the (-203), (301), (-403) and (402) planes. All these peaks are dedicated to niobium pentoxide peaks, and no impurities peaks like NbO appeared. Peak analysis verifies that the Nb₂O₅ samples are monoclinic crystalline structure due to the existence of dominant diffraction peaks according to standard cards No. (00-037-1468). The grain size of the films was 9.4 nm, its dislocation density is 11.112 and the strain value is 0.23. Figure 2 displays the transmission spectrum of the Nb₂O₅ thin film.

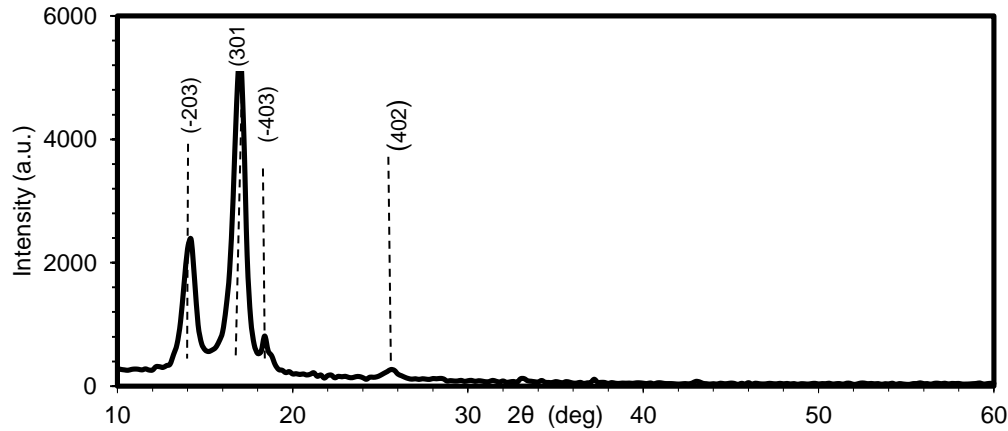


FIGURE 1. X-ray diffraction spectrum for the prepared thin film on quartz substrate

Optical transmission as a function of the incident wavelength is depicted in Fig. 2. The optical edge (shoulder) at the UV region ensures the formation of the material with its typical energy gap. Based on the transmission spectrum, the energy gap was estimated using equation (6) as portrayed in Fig. 3. Extrapolating the linear range gives the band gap of about 3.33 eV.

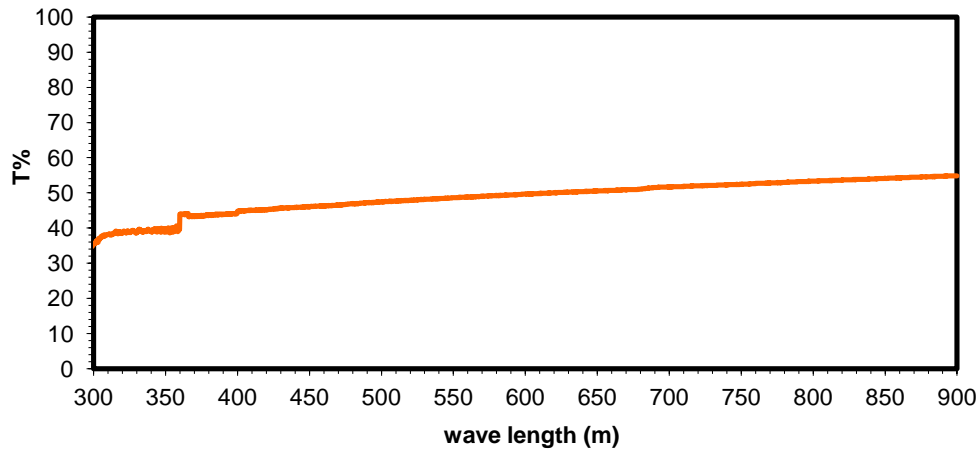


FIGURE 2. Relation between the wave length and the transmission of the prepared thin films deposited on quartz substrate

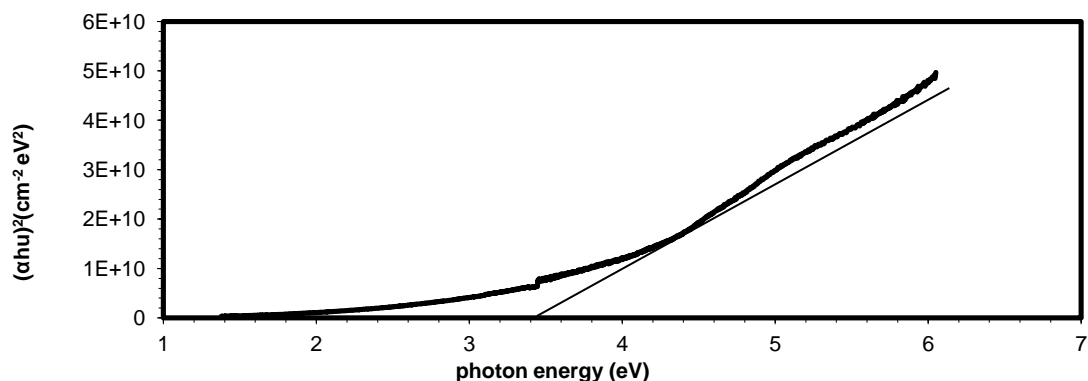


FIGURE 3. Estimated energy gap for prepared Nb₂O₅ thin films on quartz substrate

Urbach energy could be calculated from the plotted graph of the natural logarithm of the absorption coefficient and the energy of the absorbed photon. Fitting the linear part of the curve with a straight line as shown in Fig. 4 provides the value of Urbach energy.

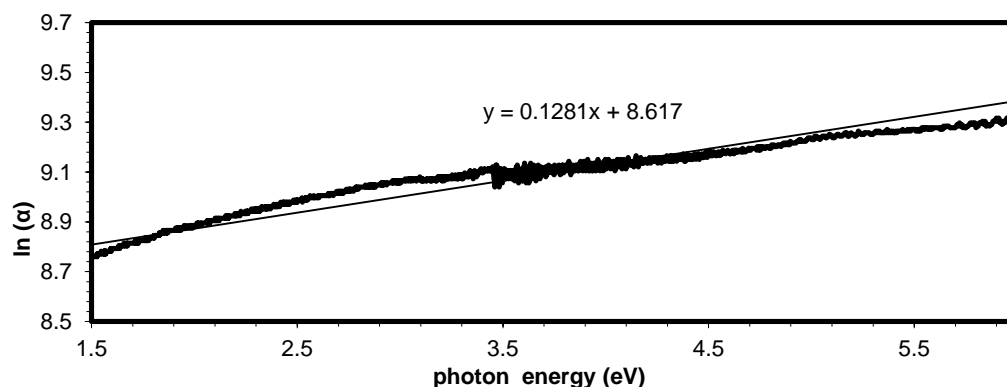


FIGURE 4. The absorption coefficient vs incident photon energy

Extinction coefficient, K and optical conductivity, σ were also estimated by using equations 8 & 9, and shown in Fig 5. The large value of K may be ascribed to structural modification in the samples. The optical conductivity is almost constant throughout with nominal value of 1×10^4 .

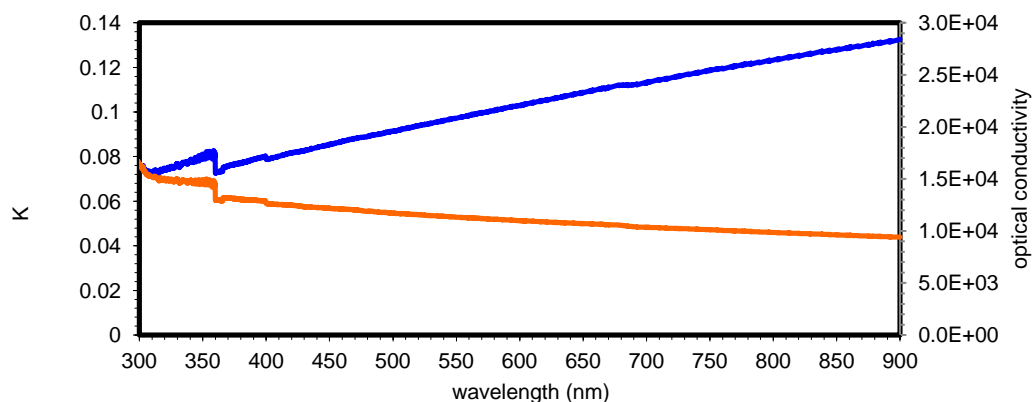


FIGURE 5. Extinction coefficient and optical conductivity as a function of wavelength

Morphological properties of the prepared Nb_2O_5 thin film deposited on the quartz substrate are presented in Fig. 6 which is ideal for the quantitatively measuring the surface roughness and expedite the perception of the crystal structures. Two and three dimensional AFM images of the films are illustrated respectively which reveals the uniformity and cracks free surface with an average particle size of 250 nm.

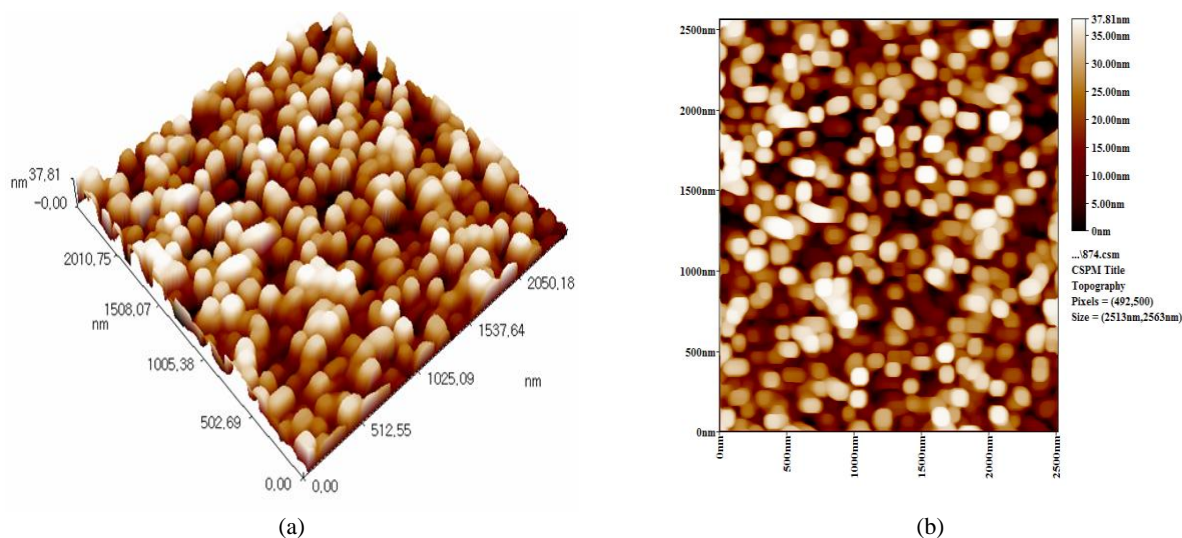


FIGURE 6. AFM images of the prepared thin film: (a) 3D image and (b) 2D image

CONCLUSIONS

According to the obtained results, it could be concluded that monoclinic Nb_2O_5 thin films may be easily prepared by employing chemical method using ammonia as a main raw material through chemical interaction with niobic acid solution. The particle size was recorded to be 250 nm with a band gap of about 3.33 eV. There are no observed impurities in the films that indicated its preparation procedure is successfully controlled. However, large extinction coefficient is recorded.

REFERENCES

1. Jian J. Wang, Yong Q. Wang, Fei F. Cao, Yu G. Guo, Li J. Wan, *J. Am. Chem. Soc.* **132**, 12218 (2010).
2. K. Chen, C. Hsu, J. Liu, Y. Liou, C. Yang, *Micromachines* **7**, 151 (2016).
3. K. Abood, E. T. Salim and J. A. Saimon, *International Journal of Nanoelectronics and Materials* **11(2)**, 127 (2018)
4. M. Baltes, A. Kytokivi, Bert M. Weckhuysen, Robert A. Schoonheydt, Pascal V. D. Voort, Etienne F. Vansant, *J. Phys. Chem. B* **105** 6211 (2001).
5. Y. Huang, X. Duan, Charies M. Lieber, *Small* **1**, 142 (2005).
6. Rozina A. Rani, Ahmad S. Zoofakar, Anthony P. O'Mullane, Micheal W. Austin, Kourosh K. Zadeh, *J. Mater. Chem. A* **2**, 15683 (2014).
7. F. Xia, T. Mueller, Y. Lin, A. Valdes-Garcia, P. Avouris, *Nat. Nanotech.* **4**, 839 (2009).
8. X. Fang, L. Hu, K. Huo, B. Gao, L. Zhao, M. Liao, Paul K. Chu, Y. Bando, D. Golberg, *Adv. Funct. Mater.* **21**, 3907 (2011).
9. Michel A. Aegerter, M. Schmitt, Y. Guo, *International J. Photoenergy* **4(1)**, 1 (2002).
10. D. Yao, Rozina A. Rani, Anthony P. O. Mullane, K. Kalantar-Zadeh, Jian Z. Ou, *J. Phys. Chem. C* **118**, 476 (2014).
11. Kimberly D. Pollard, Richard J. Puddephatt, *Chem. Mater.* **11**, 1069 (1999).
12. Mazur, M.; Szymanska, M.; Kaczmarek, D.; Kalisz, M.; Wojcieszak, D.; Domaradzki, J.; Placido, F., *Appl. Surf. Sci.* **301**, 63 (2014).
13. Forouhi, A.R.; Bloomer, I., *Phys. Rev. B* **38**, 1865 (1988).
14. S. Furukawa, Y. Ohno, T. Shishido, K. Teramura, T. Tanaka, *ACS Catal.* **1**, 1150 (2011).
15. Y. Ahn, J. Dunning, J. Park, *Nano Lett.* **5**, 1367 (2005).
16. Fiz, R. Hernandez-Ramirez, F. Fischer, T. Lopez-Conesa, L. Estrade, S. Peiro, F. Mathur, S., *J. Phys. Chem. C* **117**, 10086 (2013).
17. D. Velten, E. Eisenbarth, N. Schanne, J. Breme, *J. Mater. Sci. Mater. Med.* **15**, 457 (2004).
18. Michel A. Aegerter, *Solar Energy Materials & Solar Cells* **68**, 401 (2001).
19. Jian Z. Ou, Rozina A. Rani, M. Ham, Matthew R. Field, Y. Zhang, H. Zheng, P. Reece, S. Zhuiykov, S. Sriram, M. Bhaskaran, Riched B. Kaner, K. Kalantar-zadeh, *ACS Nano* **6**, 4045 (2012).
20. H. Luo, W. Song, Paul G. Hoertz, K. Hanson, R. Ghosh, S. Rangan, M. Kyle Brennaman, Javier J. Concepcion, Robert A. Binstead, Rpbert A. Bartynski, R. Lopez, Thomas J. Meyer, *Chem. Mater.* **25**, 122 (2013).
21. Chandiran, A. Kumar, N., Mohammad K., G. Micheal, *Advanced Functional Materials* **24**, 1615 (2014).
22. M. Suzan, P. Francisco, Y. Gushikem, *J. Mater. Chem.* **12**, 2552 (2002).
23. Matthew D. Pickett, Medeiros-Ribeiro G, R. Stanley Williams, *Nat. Mater.* **12**, 114 (2013).
24. Franklin J. Wong, S. Ramanathan, *J. Mater. Res.* **28**, 2555 (2013).
25. Matthew D. Pickett, R. Stanley Williams, *Nanotechnology* **23**, 215202 (2012).
26. Adrian A. Bolzan, Celesta Fong, Brendan J. Kennedy, Christopher J. Howard, *J. Solid State Chem.* **113**, 9 (1994).
27. K. Sakata, I. Nishida, M. Matsushima, and T. Sakata, *J. Phys. Soc. Japan* **27**, 506 (1969).
28. F. A. Chudnovskii, L. L. Odynets, A. L. Pergament, and G. B. Stefanovich, *J. Solid State Chem.* **122**, 95 (1996).
29. X. Xiao, G. Dong, C. Xu, H. He, H. Qi, Z. Fan, J. Shao, *Appl. Surf. Sci.* **255**, 2192 (2008).
30. M. K. Abood, M. H. A. Wahid, E. T. Salim, J. A. Saimon, *EPJ Web of Conferences* **162**, 01058 (2017).
31. Jae H. Lim, J. Choi, *J. Ind. Eng. Chem.* **15**, 860 (2009).
32. S. Venkataraj, R. Drese, Ch. Liesch, O. Kappertz, R. Jayavel, M. Wuttig, *J. Appl. Phys.* **91**, 4863 (2002).
33. H. Miyake, H. Kozuka, *J. Phys. Chem. B* **109**, 17951 (2005).
34. Shane A. O'Neill, Ivan P. Parkin, Robin J. H. Clark, A. Mills, N. Elliott, *J. Mater. Chem.* **13**, 2952 (2003).
35. Zaid T Salim, U Hashim, MK Md Arshad, Makram A Fakhri, Evan T Salim, *Microelectronic Engineering* **179**, 83-90 (2017).
36. M. A Fakhri, Evan T Salim, U Hashim, Ahmed W Abdulwahhab, Zaid T Salim, *Journal of Materials Science: Materials in Electronics* **28**, 16728-16735 (2017).
37. Zaid T Salim, U Hashim, MK Md Arshad, Makram A Fakhri, *Int. J. Appl. Eng. Res* **11**, 8785-8790 (2016).

38. M.. A. Fakhri , F. Hattab, Engineering Sciences (FNCES), 2012 First National Conference, IEEE, **2012**, 1-5 (2012).
39. M. A Fakhri, Evan T Salim, MHA Wahid, U Hashim, Zaid T Salim, Raid A Ismail, Journal of Materials Science: Materials in Electronics **28**, 11813-11822 (2017).
40. M.. A. Fakhri, Y. Al-Douri , Evan. T. Salim, U. Hashim, Yushamdan Yusof, Ee Bee Choo, Zaid T.Salim, Yaseen N. Jurn5 , ARPJ Journal of Engineering and Applied Sciences **11**, 4974-4978 (2016).
41. E. T Salim, Jehan A. Saimon, Marwa K Abood and Makram A Fakhri, Mater. Res. Express **4**, 106407 (2017).
42. E. T. Salem, Makram A. Fakhry, Hala Hassen, Int. J. Nanoelectronics and Materials **6**, 121-128 (2013).
43. M. A Fakhri, M Halim A Wahid, Ban A Badr, Suad M Kadhim, Evan T Salim, Uda Hashim, Zaid T Salim, EPJ Web of Conferences **162**, 01004 (2017).
44. M. A Fakhri, M Halim A Wahid, Suad M Kadhim, Ban A Badr, Evan T Salim, Uda Hashim, Zaid T Salim, EPJ Web of Conferences **162**, 01005 (2017).
45. E. T. Salim, Raid A. Ismail, Makram A. Fakhry, Yushamdan Yusof, Int. J. Nanoelectronics and Materials **9**,111-122 (2016).