Sains Malaysiana 45(8)(2016): 1207–1211

Fabrication of Flourine Doped Tin Oxide with Different Volume of Solvents on FTO Seed Layer by Hydrothermal Method

(Fabrikasi Flourin Terdop Timah Oksida dengan Jumlah Pelarut Berbeza ke atas Lapisan Benih FTO melalui Kaedah Hidroterma)

M.L. MOHD NAPI*, N. NAYAN, M.K. AHMAD, F.I.M. FAZLEE, N.K.A. HAMED & N.S. KHALID

ABSTRACT

Flourine doped tin oxide films were synthesized by using hydrothermal method with different volume of solvents. The thin film growth was carried out by fixing the concentration of tin and fluorine element precursors by only varying their solvents which were 2-propanol and DI water. The fabrication of FTO thin film by using mineral salt group as tin precursor with hydrothermal method on soda lime glass showed that the nanostructured growth did not distribute largely and took longer time. The seed layer of FTO has been used to overcome these problems thus the thin film growth distributed largely in short time. These experiments were conducted at a constant of hydrothermal temperature and reaction time which were 150°C and 5 h respectively. The result showed that, there was a change on the surface morphology in the formation of FTO films. The minimum value of sheet resistance was 0.1475 Ω/sq which was obtained using 65 mL of 2-propanol and 20 mL of DI water was lower than sheet resistance of commercial FTO films of 01693 Ω/sq. This fabricated FTO films showed a good transparency with higher of transmittance than 80%. The experimental findings suggested that 65 mL amount of 2-propanol and 20 mL of DI water in precursor solutions could produce the better of FTO performance than commercial FTO.

Keywords: Electrical properties; hydrothermal method; nanoparticle; thin film; water

ABSTRAK

Flourin terdop timah oksida telah disintesis menggunakan kaedah hidroterma dengan pelbagai jumlah isi padu pelarut. Pertumbuhan filem nipis dijalankan dengan mengekalkan kepekatan unsur timah dan flourin dengan hanya mengubah isi padu pelarut iaitu 2-propanol dan air suling. Fabrikasi filem nipis FTO dengan menggunakan kaedah hidroterma di atas sampel kaca kosong telah menunjukkan bahawa pertumbuhan struktur nano tidak menyeluruh dan mengambil masa yang lama. Lapisan benih FTO telah digunakan untuk mengatasi masalah ini seterusnya menghasilkan pertumbuhan filem nipis yang menyeluruh dalam masa yang singkat. Penyelidikan ini dijalankan dengan mengekalkan suhu hidroterma iaitu 150°C selama 5 jam bagi tempoh reaksi. Hasil kajian menunjukkan terdapat perubahan pada sifat permukaan bagi pembentukan filem nipis FTO. Nilai rintangan minimum helaian ialah 0.1475 Ω/sq yang diperoleh dengan menggunakan isi padu pelarut sebanyak 65 mL 2-propanol dan 20 mL air ternyahion yang lebih rendah nilainya jika dibandingkan dengan nilai rintangan helaian bagi FTO komersial iaitu sebanyak 0.1693 Ω/sq. Filem nipis FTO yang difabrikasi ini menunjukkan sifat kelutsinaran yang baik iaitu nilai kepancaran yang lebih tinggi daripada 80%. Hasil kajian mencadangkan bahawa dengan menggunakan 65 mL 2-propanol dan 20 mL air ternyahion dalam larutan pelopor boleh menghasilkan perilaku FTO yang lebih baik berbanding FTO komersial.

Kata kunci: Air; filem nipis; kaedah hidroterma; sifat elektrik; zarah nano

INTRODUCTION

SnO_2 is a n-type semiconductor with a wide band gap energy of 3.62 eV and is well known as a transparency material in the visible region and reflecting in the high infrared region (Kong et al. 2009). The conductivity of SnO_2 could be enhanced by doping with group III, V, VI and VII elements of the periodic table, some of which were Tl, Sb, Te and F. Flourine is the most preferred because the resultant fluorine doped tin oxide (FTO) film is highly stable both chemically and thermally (Ghafouri et al. 2012; Yadav et al. 2009). The FTO nanostructures can be synthesized by several methods which are spray deposition pyrolysis (Moholkar et al. 2007), chemical vapour deposition (Fang & Chang 2003), inkjet printing (Samad et al. 2011), pulsed laser deposition (Chen et al. 2005) and hydrothermal method (Mohd Khairul & Murakami 2012). These thin films have been successfully demonstrated as transparent conducting oxide, low-emissivity windows in buildings, flat panel displays, electrochromic mirrors and windows, defrosting windows, oven windows, static dissipation, touch-panel control and electromagnetic shielding (Gordon 2000).

In previous works, we found that the synthesis of nanostructure using hydrothermal method was beneficial to fabricate small distribution of grain size and take a long reaction time (Wu et al. 2010). Recent report about fabrication of FTO using hydrothermal method only focused on mineral salt group as tin precursor such as tin (ii) chloride and tin (iv) chloride (Wang et al. 2014, 2012) and there is no widely deep researches about fabrication of FTO films using organonmetallic compound like di-*n*-butyl-tin(IV) diacetate (DBTDA), tetra-*n*-butyl-tin (TTBT) and tri-*n*-butyl-tin diacetate TBTA as tin precursor that have the ability to decompose and less well edges give advantage in optical and electrical properties compared to mineral salts group as tin precursor (Zhao et al. 2008). The variety of solvents used also play an important roles for the layers to have different surface, sheet resistance and transparency which also depend on type of method that was used (Smith et al. 1998). A literature survey can be concluded that the surface morphology of FTO thin film depends on the solvent which has high atomizing rate (Smith et al. 1998). Hence, to achieve a better control of the thin film growth, a few reports using 2-propanol as solvent showed the lowest sheet resistance of FTO produced and the chosen of solvents pair which are 2-propanol with water by using spray pyrolysis deposition method that tend to get high transparency of FTO thin films (Moholkar et al. 2008, 2007).

In this paper, we investigated the growth of FTO on seed layer with varying amount of solvents pair which were 2-propanol and DI water using hydrothermal method. Using constant concentration of dibutyltindiacetate (DBTDA) as tin precursor and ammonium fluoride (NH_4F) as fluorine element this experiment was conducted in 150°C of hydrothermal temperature and 5 h reaction time. The surface morphology, electrical and optical properties were studied and discussed.

MATERIALS AND METHODS

The FTO films were deposited from 0.2M of DBTDA dissolved in 2-propanol and 0.6 M of NH_4F dissolved in deionized water (DI water). Then, both solution were mixed together. DBTDA is not soluble in water. In order to study the effect of solvent pair amount, four solutions with different amount (mL) of solvent (2-propanol (P)/DI water (W)) were used. These contents were 85 mL(P)/0 mL(W), 65 mL(P)/20 mL(W), 45 mL(P)/40 mL(W) and 25 mL(P)/60 mL(W). Each precursor solution was stirred for 30 min. The FTO substrates were cleaned using deionized water, acetone and ethanol with volume ratio of 1:1:1 in an ultrasonic cleaner to eliminate foreign material at substrates. As shown in Figure 1, the FTO glass substrates were placed on the sample stage and the stock solution was poured gently into the autoclave before it was put into the oven. The hydrothermal synthesis was conducted at 150°C of hydrothermal temperature in 5 h constantly.

The deposited thin films were characterized to study their surface, electrical and optical properties. The surface morphology of FTO films was studied using field emission scanning electron microscopy (FESEM-JOEL-JSM-7600F) to identify the distribution of grain, grain size and the growth of nanostructured with preferred orientation. The thickness of the film was calculated by (1) (Moholkar et al. 2007) where n_o, n_1 and n_2 stands for the refractive index of air (n_0 =1.0002778) (Ciddor 1996); SnO_2 (n_1 = 2.8) (Saturi et al. 2012) and soda lime glass (n_2 =1.51) (Saturi et al. 2012), respectively; is thickness of thin film; and T refer for the transmittance percentage at wavelength, λ = 550 nm.

$$T = \frac{t_1^2 t_2^2}{1 + 2r_1 r_2 \cos 2\delta + r_1^2 r_2^2} \times \frac{n_2}{n_o}, \qquad (1)$$

Where $r_1 = \frac{n_0 - n_1}{n_0 + n_1}$, $r_2 = \frac{n_1 - n_2}{n_1 + n_2}$, $t_1 = \frac{2n_0}{n_0 + n_1}$, $t_2 = \frac{2n_1}{n_1 + n_2}$ and $\delta = \frac{2nn_1 d}{\lambda}$.

The optical properties were studied using UV-VIS Spectrophotometer (UV-1800 spectrophotometer) to investigate the visible transmittance in 350-800 nm wavelength. The electrical properties were measured using two point probe method and connected to source meter Ariel IV Test Station.

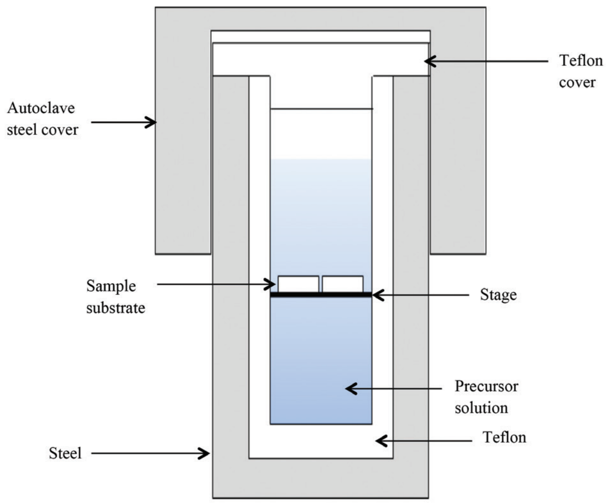

FIGURE 1. Schematic representation of an autoclave and sample prepared

RESULTS AND DISCUSSION

SURFACE MORPHOLOGY

Surface morphology of commercial FTO films and FTO films that have been prepared were examined using FESEM analysis. Figure 2 shows the images of layer surface of commercial FTO films and FTO films prepared at 100 k magnification and 25 k magnification for inset of each images. Figure 2(a) displays the nanoparticles of commercial FTO films with the pinholes that can be seen clearly on the inset image 2(a). The commercial FTO films are less compact of FTO. Figure 2(b) indicates that the grain size of FTO nanoparticles were increased when the experiment is conducted using the highest amount of 2-propanol. The nanoparticles then densely packed without the pinholes due to increment of grain size that can be seen clearly on the inset image in Figure 2(b). In Figure 2(c), on the larger grain size of FTO, the new small FTO nanostructure was attached due to adhering process which was the small nanocrystal of FTO would attach on larger particle size and aligned at location (Dou et al. 2011). Inset in Figure 2(c) shows a few pinholes exist and make the gap between the grain boundaries. Figure 2(d) and 2(e) shows that the grain size of FTO nanoparticle start to decrease thus the pinhole size increase largely at the layer surface with respect to the water amount. The increments of pinhole size make the FTO nanostructure only grow at a few portion of surface. Depicted the FTO film started to decompose when the amount of DI water increase. The growth rate of FTO thin film is related to the amount of DI water contain in precursor solution, the higher water amount that has been used would slower the growth rate of the thin film (Zhao et al. 2008).

OPTICAL PROPERTIES

Table 1 shows the thickness of FTO film prepared from different volume of solvents by using (1). The thickness of FTO films decreased with respect to the increase of DI water volume. For sample (b), the highest quantity of the alcohol in the solution was able to increase the thickness of the thin film (Moholkar et al. 2007) and from the surface morphology this sample showed that the distribution of grain size became more packed without the pinholes. In this paper, the increasing amount of water as solvent would decrease the thickness of the thin film. Even for sample (c) where the new nanostructures of FTO grown on the larger grain size the film was still thin. The change of the pinholes size to the larger by the amount of DI water level gave more evidence that DI water is affecting the process of decomposing of FTO films.

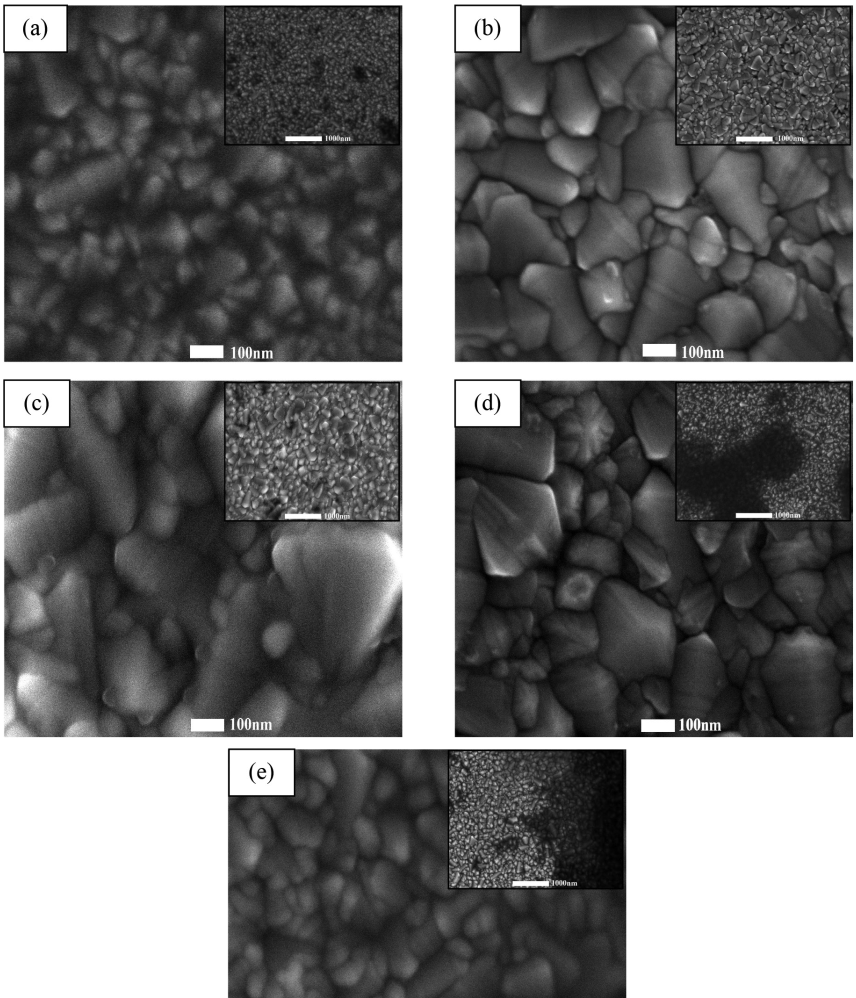

FIGURE 2. FESEM surface view of FTO with different amount of solvent at 100 k magnification and 25 k magnification for each inset a) Commercial FTO, b) 85 mL(P)/0 mL(W), c) 65 mL(P)/20 mL(W), d) 45 mL(P)/40 mL(W) and e) 25 mL(P)/60 mL(W)

TABLE 1. The resistance and sheet resistance of FTO seed layer and FTO prepared on seed layer with different volume of solvents

Sample (P – 2Propanol/ W- water) (mL)	Resistance (Ω)	Sheet resistance (Ω/sq)	Thickness (nm)
a) Commercial FTO	0.08465	0.1693	595
b) 85 mL(P)/0 mL(W)	0.08565	0.1713	686
c) 65 mL(P)/20 mL(W)	0.07377	0.1475	541
d) 45 ml(P)/40 mL(W)	0.08802	0.1760	487
e) 25 mL(P)/60 mL(W)	0.09675	0.1935	339

Figure 3 shows the transmittance of FTO thin film deposited on FTO seed layer using visible wavelength (300-800 nm) from UV-VIS spectrophotometer. From Figure 3, it can be seen from the plots that all the FTO films that has been prepared were highly transparent over 500-800 nm in range 75-90%. The result showed that the properties of good transparent material and thus suitable to apply as transparent conducting oxide (TCO). From the plot, the sample that used the highest amount of DI water has the highest percentage of transmittance due to the thinnest layer of that sample. Thus the light would able to pass through the FTO films that related to low optical scattering as reported by Premalal et al. (2012a). Sample (b) which has the highest thickness of film and as mentioned in previously showed that the FTO films with packed dense nanostructure showed the lowest transmittance compared to others. However, this sample was still in high transparent to be apply as transparent conducting oxide (TCO).

As shown in the Figure 3, the light with wavelength below 400 nm was absorbed by all films. At this stage, the electron transition from the valence band to the conduction band has absorbed the ultraviolet light (Zhao et al. 2008).

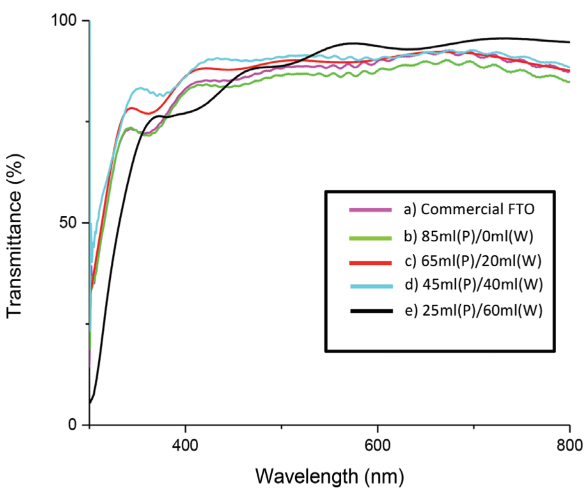

FIGURE 3. The transmittance versus wavelength plots of FTO prepared with different volume ratio of solvents

ELECTRICAL PROPERTIES

Table 1 shows the electrical properties analysis of FTO films obtained by using two point probe method. It shows that the commercial FTO films have the sheet resistance of 0.1693 Ω/sq. After the fabrication process of FTO on this seed layer with different volume of solvents, sample (c) appeared to have the lowest sheet resistance compared to the entire sample including sample (a). The sheet resistance depends on thickness, grain size and surface morphology. If we compared sample (c) with sample (b) and (a), the thickness and the existence of small particles attached to the large grain size which is the point address in FESEM analysis make the sheet resistance lower than sample (b) and (a). The thinner layer of thin film caused the electrons to easily cross over the grains. Another reason is that sample (c) has larger grain size. The larger grain size lead to lesser grain boundaries and the electron can pass or travel without high resistance (Premalal et al. 2012b).

The sheet resistance and resistance of the thin film decrease with respect to the thickness (Batzill & Diebold 2005), but in this work the reverse situation occurred which is the thinner layer of thin film of sample (e) produce the high sheet resistance as compared to the thicker one. This situation occurred because sample (e) has the existence of pinholes with the largest size compared to others. These pinholes caused difficulty for electron to flow from single nanocrystal to others, thus the current has difficulty to flow through. Therefore, the sheet resistance and resistance were higher for the material. With the high amount of DI water, the film contain large pinholes and thus the mobility of the carrier in the film would be slowed due to the decreasing of grain boundary that caused by the decomposition process.

CONCLUSION

FTO films were prepared on bare FTO substrates by hydrothermal method. By varying the volume of solvent, the best films was obtained in sample that has been conducted using 65 mL of 2-propanol and 20 mL of DI water which has the minimum sheet resistance of 0.1475 Ω/sq with 80% of transmittance. This FTO films was prepared using 65 mL of 2-propanol and 20 mL of DI water has better performance compared to commercial FTO based on the value of sheet resistance and its transparency percentage.

ACKNOWLEDGEMENTS

This work was financially supported by the *Exploratory Research Grant Scheme* (ERGS) vote number E022. The authors gratefully thank all the members of Solar Cell Laboratory and MiNT-SRC UTHM for the technical support.

REFERENCES

Batzill, M. & Diebold, U. 2005. The surface and materials science of tin oxide. *Progress in Surface Science* 79(2): 47-154.

Chen, Z.W., Lai, J.K.L. & Shek, C.H. 2005. Multifractal spectra of scanning electron microscope images of SnO_2 thin films prepared by pulsed laser deposition. *Physics Letters A* 345(1): 218-223.

Ciddor, P.E. 1996. Refractive index of air: new equations for the visible and near infrared. *Applied Optics* 35(9): 1566-1573.

Dou, X., Sabba, D., Mathews, N., Wong, L.H., Lam, Y.M. & Mhaisalkar, S. 2011. Hydrothermal synthesis of high electron mobility Zn-doped SnO_2 nanoflowers as photoanode material for efficient dye-sensitized solar cells. *Chemistry of Materials* 23(17): 3938-3945.

Fang, T.H. & Chang, W.J. 2003. Effect of freon flow rate on tin oxide thin films deposited by chemical vapor deposition. *Applied Surface Science* 220(1): 175-180.

Ghafouri, V., Shariati, M. & Ebrahimzad, A. 2012. Photoluminescence investigation of crystalline undoped ZnO nanostructures constructed by RF sputtering. *Scientia Iranica* 19(3): 934-942.

Gordon, R.G. 2000. Criteria for choosing transparent conductors. *MRS bulletin* 25(08): 52-57.

Kong, J., Deng, H., Yang, P. & Chu, J. 2009. Synthesis and properties of pure and antimony-doped tin dioxide thin films fabricated by sol-gel technique on silicon wafer. *Materials Chemistry and Physics* 114(2): 854-859.

Mohd Khairul bin Ahmad & Murakami, K. 2012. Low temperature and normal pressure growth of rutile-phased TiO_2 nanorods/nanoflowers for DSC application prepared by hydrothermal method. *Journal of Advanced Research in Physics* 3(2): 021208.

Moholkar, A.V., Pawar, S.M., Rajpure, K.Y., Almari, S.N., Patil, P.S. & Bhosale, C.H. 2008. Solvent-dependent growth of sprayed FTO thin films with mat-like morphology. *Solar Energy Materials and Solar Cells* 92(11): 1439-1444.

Moholkar, A.V., Pawar, S.M., Rajpure, K.Y. & Bhosale, C.H. 2007. Effect of solvent ratio on the properties of highly oriented sprayed fluorine-doped tin oxide thin films. *Materials Letters* 61(14): 3030-3036.

Premalal, Edirisinghage VA, Dematage, N., Kaneko, S. & Konno, A. 2012a. Development of quality FTO films by spray pyrolysis for dye-sensitized solar cell. *Electrochemistry* 80(9): 624-628.

Premalal, EVA, N Dematage, S Kaneko, and A Konno. 2012b. Preparation of high quality spray-deposited fluorine-doped tin oxide thin films using dilute di (n-butyl) tin (iv) diacetate precursor solutions. *Thin Solid Films* 520(22): 6813-6817.

Samad, Wan Zurina, Muhamad Mat Salleh, Ashkan Shafiee, and Mohd Ambar Yarmo. 2011. Structural, optical and electrical properties of fluorine doped tin oxide thin films deposited using inkjet printing technique. *Sains Malaysiana* 40(3): 251-257.

Saturi Baco, Abdullah Chik & Fouziah Md Yassin. 2012. Study on optical properties of tin oxide thin film at different annealing temperature. *Journal of Science and Technology* 4(1): 61-72.

Smith, Agnes, Jean-Marc Laurent, David S Smith, and Jean Pierre Bonnet. 1998. Experimental survey of different precursor/solvent pairs for the deposition of tin dioxide by pyrosol. *Thin Solid Films* 315(1): 17-21.

Wang, H., Fang Fu, Feihu Zhang, Hong-En Wang, Stephen V. Kershaw, Jiaqiang Xu, Shi-Gang Sun, and Andrey L. Rogach. 2012. Hydrothermal synthesis of hierarchical SnO_2 microspheres for gas sensing and lithium-ion batteries applications: Fluoride-mediated formation of solid and hollow structures. *Journal of Materials Chemistry* 22(5): 2140-2148.

Wang, H., Kalytchuk, S., Yang, H., He, L., Hu, C., Teoh, W.Y. & Rogach, A.L. 2014. Hierarchical growth of SnO_2 nanostructured films on FTO substrates: structural defects induced by Sn (II) self-doping and their effects on optical and photoelectrochemical properties. *Nanoscale* 6(11): 6084-6091.

Wu, S., Yuan, S., Shi, L., Zhao, Y. & Fang, J. 2010. Preparation, characterization and electrical properties of fluorine-doped tin dioxide nanocrystals. *Journal of Colloid and Interface Science* 346(1): 12-16.

Yadav, A.A., Masumdar, E.U., Moholkar, A.V., Rajpure, K.Y. & Bhosale, C.H. 2009. Effect of quantity of spraying solution on the properties of spray deposited fluorine doped tin oxide thin films. *Physica B: Condensed Matter* 404(12): 1874-1877.

Zhao, H., Liu, Q., Cai, Y. & Zhang, F. 2008. Effects of water on the structure and properties of F-doped SnO_2 films. *Materials Letters* 62(8-9): 1294-1296.

Microelectronics and Nanotechnology
Shamsuddin Research Centre (MiNT- SRC)
Universiti Tun Hussein Onn Malaysia
86400 Batu Pahat, Johor Darul Takzim
Malaysia

*Corresponding author; email: mluqmannapi@gmail.com

Received: 20 April 2015
Accepted: 18 November 2015