

MODIFICATION OF BSF LAYER IN BIFACIAL SOLAR CELL VIA PHOTSENSITIZATION OF MOLECULES NANOSTRUCTURE

Nurul Aqidah Mohd Sinin, Mohd Adib Ibrahim*, Suhaila Sepeai, Mohamad Yusof Sulaiman, Mohd Asri Mat Teridi, Norasikin Ahmad Ludin, Saleem H. Zaidi

Solar Energy Research Institute, Universiti Kebangsaan Malaysia, 43600 Bangi Selangor, Malaysia

Article history

Received

15 June 2015

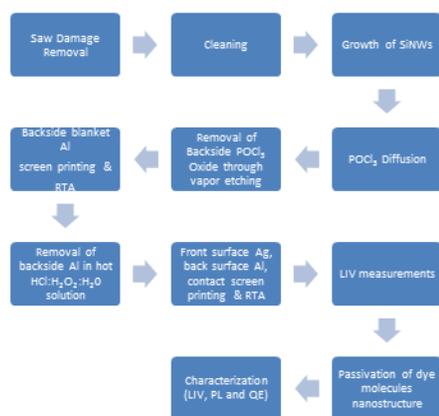
Received in revised form

19 September 2015

Accepted

21 December 2015

*Corresponding author
mdadib@ukm.edu.my



Abstract

Surface passivation is the most significant step to keep the recombination loss at a tolerable minimum and avoid an unacceptably large efficiency loss when moving towards thinner silicon material. In this study, the modification and photosensitization on back surface field (BSF) of bifacial solar cell was investigated by using dye molecules nanostructure namely DiO. The DiO dye molecules nanostructure was passivated on SiNW and BSF layers using spin-coating method. The energy gaps of DiO dye are 2.14 eV (DiO in chloroform), 2.13 eV (DiO on silicon nanowire (SiNW)) and 2.12 eV (DiO on BSF). The time resolved photoluminescence increased with the DiO dye coated on SiNW ($\tau = 1.24$ ns) and BSF layers ($\tau = 0.93$ ns) compared to DiO dye in chloroform ($\tau = 0.54$ ns). The light trapping inside the interface layers of DiO dye/silicon indicating a slow process of charge recombination before its reach equilibrium states, it is due to interface interaction bonding within boundary layers and dye molecules nanostructure. The short circuit current density also increased about 25% from 4.44 to 5.56 mA/cm² when applying the dye molecules nanostructure on BSF of the cell. Collection of photo carrier lead of internal and external quantum efficiency improved about 19% and 25%, respectively, is mainly due to energy transported to the junction. The photo-generated electron on DiO dye lead to improvement in the exciton dissociation efficiency leading to increase in the electrical properties.

Keywords: Bifacial solar cell, back surface field, molecules nanostructure, quantum efficiency, time resolved photoluminescence

© 2016 Penerbit UTM Press. All rights reserved

1.0 INTRODUCTION

Bifacial solar cells are designed to allow light to enter from both front and rear sides. The main issues in back surface were identified such as low efficiency, low photo generated current and recombination losses. The recombination losses occurred due to the low quality of back surface field (BSF) layer, poor passivation and also due to wafer thickness. Doped junctions on the back surface are a well-known technique to reduce back-surface recombination in

crystalline silicon solar cells. These junctions are commonly known as back-surface fields (BSF). A BSF consists of a higher doped region at the rear surface of the solar cell. Alloying with aluminum (Al), screen-printed layer of Al or boron diffusion on *p*-type wafers are a few methods to form a BSF layer. This introduces a *p*⁺-*p* junction and presents a potential barrier to the minority electron [1]. This BSF reflects electrons and reduces the effective rear surface recombination velocity. The extra *p*⁺-*p* junction also adds to the built-in bias of the cell, and may enhance the open-circuit

voltage (V_{oc}). The interfaces between this layer and the relatively lightly doped bulk region of the cell acts as a low recombination velocity surface [2].

The effective passivation techniques can reduce the effect of surface recombination in silicon. Generally, surface passivation using inorganic materials, such as silicon nitride (SiN) and silicon dioxide (SiO₂), has been widely used for realizing high-efficiency crystalline silicon solar cells [3]. The function of surface passivation layer is to provide good dielectric properties, low surface recombination velocity, controlled immobile charge density, and device stability at elevated temperature under standard operating conditions. Unfortunately, passivation using SiO₂ is not suitable for low-cost industrial processes as it requires high temperature and also produce low reflective index (1.46) [4], while passivation using SiN requires high frequency to provide a much better surface passivation and UV stability albeit at the cost of hazard gas processing.

Considering these limitations, an alternative approach has been investigated based on inexpensive wet-chemical passivation. A wet-chemical passivation is organic functionalization of non-oxidized silicon surface with self-assembled monolayers bonded via a covalent Si-C bond on the hydrogen terminated (H-terminated) interface [5-7]. This modification of surface can have the possibility in controlling surface potential and surface recombination velocity in silicon [7]. Recent study on chemical passivation was take place on BSF of crystalline silicon solar cells through H-terminated by hydrofluoric acid (HF) treatment [8]. The findings showed that the HF treatment has improved the BSF performance of lifetime through short-circuit current density (J_{sc}) and V_{oc} . Although the treatment of H-terminated silicon (Si-H) shows a very low surface recombination but these surfaces worsen rapidly and are unsteady upon exposure to ambient air, as reported by previous literatures [9,10].

Alternatively, the deposition of the functionalized layers with high density of molecules nanostructures using dye fluorescence, through Langmuir Blodgett technique improved further the surfaces properties [11-13]. The modification of dye fluorescence on a silicon interface is observed through the fluorescent intensity of cyanine dyes embedded on silicon surface as a function of the distance between silicon surface and dyes layer. Monolayer of fatty acid is used as inert "spacers" to hold luminescent dye monolayers at precisely adjustable distances from the interface with an interacting medium [14]. The study showed that the dye fluorescence layer on silicon surface increase with the distance of surface with dye layers due to significant energy transfer between the silicon surface and the interface bonding of dye.

The effectiveness of energy transfer on dye molecules near the silicon surface has proven, but its application on solar cells has not been widely researched to improve the back surface of bifacial solar cell. In this paper, the improvement on the BSF by passivating using the highly fluorescent cyanine dye molecule 3,3'-dioctadecyloxacarbocyanine

perchlorate (DiO) as the molecules nanostructure was investigated. The fluorescent DiO dye cyanine molecule was passivated on the SiNW surface and BSF layer using spin-coating technique. The lifetime measurements via photoluminescence (PL) spectroscopy characterized the energy gap and degree of photosensitization. This approach can potentially lead to efficient light absorption and improve energy conversion within a compact device with inexpensive material requirement.

2.0 EXPERIMENTAL

The *p*-type <100> Si wafers with resistivity ranging between 3.0 – 6.0 Ω-cm were used. The Si wafer was initially cleaned by etching in 10 % potassium hydroxide (KOH) solution at a temperature of 70 °C for 10 minutes to remove saw damage. After rinsing with deionized (DI) water, the wafer was immersed into hydrofluoric acid (HF) and water (H₂O) solution at a ratio of 1:50 for 1 minute. Next, the wafer was dipped into HF and nitric acid (HNO₃) in a ratio of 1:100 for 10 minutes. After rinsing with DI water, it was then repeatedly immersed in HF:H₂O solution to ensure formation of hydrophobic surfaces.

The wafers were subsequently textured using a metal-assisted chemical etching (MACE) method. In this study, silicon nanowires (SiNW) were grown on the silicon surface by following methodology described by Jia *et al.* [16], based on a mixture of AgNO₃ and HF at room temperature. A mixture of AgNO₃ (0.02M) and HF (5M) was added to the cell to be etched. The etching process was done for 20 minutes and the sample rinsed thoroughly with DI water. The Si surface consisted of nano and microstructure pillars as well as silver dendrites. To remove these impurities, a cleaning procedure consisting of 2-min immersing in concentrated 65 % of HNO₃, followed rinsing with DI water several times and 8-min dipping in 5 % HF to remove the oxide layer on the sample surface. The cleaned wafers with SiNWs were subjected to the *n*-type diffusion process. The heavily doped *n*⁺-region was formed on the SiNWs wafer surface by using phosphorus oxytrichloride (POCl₃) solution as diffusion source at a temperature of 875 °C and time of 30 minutes. The oxide on the backside of the wafer was then removed by means of vapour etching (HF) for 90 seconds.

For bifacial solar cells with Al-BSF, Al pastes were screen-printed onto the backside of the Si wafer. Al paste used was purchased from FERRO Electronic Material. Following Al paste screen printing, wafers were annealed at 100 °C for 10 minutes. Subsequently, the Al BSF was created by high temperature processing in six-zone rapid thermal annealing (RTA) furnace at 850 °C to form Al-diffused *p*⁺ layer. The excess of Al was etched off in a solution of hydrochloric acid (HCl) and hydrogen peroxide (H₂O₂) at 30°C. In this way, the *n*⁺*pp*⁺ structure was successfully fabricated. Finally, the metallization processes were carried out using screen-printing of Ag

and Al pastes by employing identical grid masks on the front and back surfaces, respectively. Both contacts were fired simultaneously at 850 °C.

The finished solar cells were passivated with molecules nanostructure layer. The fabrication process of bifacial solar cell with dye molecules nanostructure was summarized in Figure 1. Hexamethyldisilazane (HMDS) was used to silylate the exposed surface of wafers to make them hydrophobic. A few drops of HDMS solution were placed in a close container and then left overnight. Simultaneously, 0.015M DiO dye was prepared by diluting it in chloroform solution. Then, the DiO was passivated on the back surface using spin-coating technique.

The device was experimentally analyzed using photoluminescence (PL) spectroscopy to measure the emission spectrum and the lifetime decay of the dyes. With the known emission wavelength, the energy gap can be determined using Eq. 1 [17],

$$E_{gap} = hc/\lambda \tag{1}$$

where E_{gap} is energy gap, h is Planck constant, c is the speed of light and λ is the peak wavelength of the PL. Time-resolved PL response was then plotted and the average lifetime was determined using Eq. 2:

$$\tau = \frac{B_1 t_1^2 + B_2 t_2^2}{B_1 t_1 + B_2 t_2} \tag{2}$$

where t_1 and t_2 represent the time constants, and B_1 and B_2 represent the amplitudes of the fast and slow components, respectively. The performance of surface modification layer was evaluated by applying to bifacial solar cell. The performance of molecular nanostructure was measured by Light Current-Voltage (LIV) and Quantum Efficiency measurements using Photovoltaic SR-EQE-IQE mapping system.

3.0 RESULTS AND DISCUSSION

3.1 Optical Characterization of Dye Molecules Nanostructure

The measurement of the band gap of materials is significant since it is directly related to its electronic properties. Silicon is an indirect bandgap semiconductor ($E_g \approx 1.12$ eV), which causes it to be a very weak light absorption. The energy gap of silicon has evidently improved by the chemical treatment of etching method [17]. Proper control of etching process made the surface nanoporous holes in it microstructure and improved the refractive index. Evidently, etching treatment to form porous in silicon has exhibits energy gap in range 1.93 - 1.95eV [18]. The energy gap was determined using Eq. 1 and plotted in Figure 2. With the excitation peak as a reference, the energy gap of DiO dye exhibits higher energy gaps of 2.14 eV (DiO in chloroform), 2.13 eV (DiO on SiNWs)

and 2.12 eV (DiO on BSF). Even though the energy gap of chemically treated silicon is higher than silicon bandgap, it is indicating the absorption region of the dye nanostructures still within the visible region of the solar irradiance. Therefore, the use of dye molecules nanostructure on different interface layers of the silicon can be works as light absorbing layers.

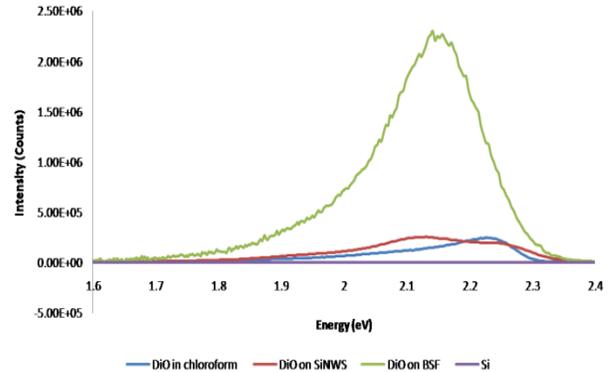


Figure 2 PL spectra intensity curve with energy

In order to clarify the role of DiO dye on different interface layers, the time resolved PL spectroscopy examined at a wavelength of 577 nm with the emission and excitation graphs in Figure 3. The emission and excitation wavelength for DiO dye is about 400 – 600 nm. Figure 2 shows the time resolved PL decay of the DiO on SiNW and BSF layers, which were fitted by single-exponential decay function (DiO in chloroform used as references). The lifetime decay of DiO dyes on different interface layers determined using Eq. 2 are summarized in Table 1.

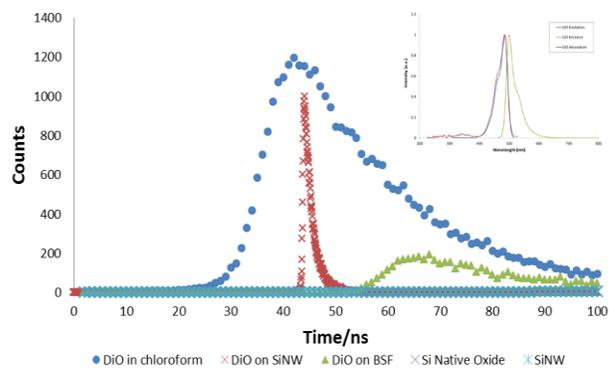


Figure 3 Time resolved photoluminescence curve for DiO in chloroform and on different substrate of Si

The measured PL decay lifetime of DiO on SiNW and BSF layers about 1.24 ns and 0.93 ns, respectively meanwhile no peak observed for single SiNW and Si native oxide samples. The lifetime decay of DiO on SiNW recorded slightly slower compare to DiO dye on BSF even though the concentrations of dye DiO (0.015M) used in this experiment were the same. It is

performed better compared to DiO in chloroform ($\tau = 0.54$ nm). Based on this result, the dye was seen to be more efficient in causing the exciton to dissociate at the interface of DiO on SiNW and BSF. This is presumable because the interface formed by the bonding between the boundary layers and the dye molecules nanostructure was well passivated. The light trapping inside the interface layers of DiO dye/silicon showed a slow process of charge recombination to establish equilibrium between the surface states and the space charge region.

The fluorescence lifetime of dye monolayer significantly shortened when present close to the silicon surface signifying efficient energy transfer as reported by Danos *et al.* [11-13]. Precise control of dye thickness is important to provide an estimate of the distance for the dye monolayer to the silicon surface via Langmuir-Blodgett technique. In spin-coated method, the precise control of the dye thickness is very challenging and requires detailed investigation with respect to variation of spin speed and dye concentration. As preliminary findings, the lifetime decay of DiO dye on SiNW and BSF is 40 ~ 50% much slower than DiO in the chloroform.

Table 1 The determination of lifetime via time resolved PL spectroscopy

Sample	B ₁	B ₂	t ₁	t ₂	X ²	τ
DiO in chloroform	0.035	0.001	0.483	1.266	1.162	0.54
DiO dye on SiNWs	0.749	0.006	0.066	1.213	1.446	1.24
DiO dye on BSF	0.016	0.004	0.332	1.466	0.908	0.93

3.2 Application Dye Molecules on Al-BSF of Bifacial Solar Cell

A 3cm × 3cm area of bifacial solar cell with aluminium-back surface field (Al-BSF) was fabricated. The DiO dye was passivated on the back surface of the solar cell using spin-coating technique.

Table 2 summarizes the electrical performance of the bifacial solar cell before and after passivation of dye layer. It is observed that the fill factor (*FF*) and *J_{SC}* for BSF with dye layer is increased by about 60% and 25%, respectively; the *V_{OC}* remained the same after and before the passivation of the dye layer. The overall electrical performance of the device (fill factor) is quiet low due to lack of optimized solar cell processing [20]. However, the *J_{SC}* has improved with the presence of the dye on the BSF. Upon illumination on the BSF, the photo-generated electrons on DiO dye would move away from the BSF layer leading to improve exciton dissociation efficiency. This results in the *J_{SC}* increasing from 4.44 to 5.56 mA/cm².

Here, the mechanism of photosensitization through dye molecules occurred when the dye molecule (act

as the sensitizer) absorbs the photons. Light absorbed in surrounding dye molecules results in free electrons in the DiO/silicon interface layer, apparently unbound from traps by energy transfer from 'trapped excitons' on the back surface. Energy transfer can also produce electron-hole pairs in a semiconductor. Dexter [15] proposes the generation of electron-hole pairs in a semiconductor by non-radiative energy transfer from dye molecules on the silicon surface.

Table 2 Summarized of electrical performance of BSF with and without dye layer

Sample	<i>V_{OC}</i> (V)	<i>J_{SC}</i> (mA/cm ²)	<i>FF</i>
Back surface without dye	0.23	4.44	0.21
Back surface with dye	0.23	5.56	0.34

Determination of dye energy gap (see Figure 2) would support on how the *J_{SC}* is improved. The dye energy gap (2.12 eV) is matched to flat band regions. The electron minority carrier's population generated at BSF is now significantly modified by illumination. In such flat band regions, the excess minority is generated under illumination that needs to be brought to the built-in electrostatic region. With this situation, the photo-generated of minority carriers need to travel large lateral distances before being collected (in this case of bifacial solar cell). Therefore, the role of surface modification and photosensitization using dye molecules sensitization has enhanced the electrical performance of the device.

3.3 Quantum Efficiency Measurements

In silicon solar cell, quantum efficiency indicates the amount of current that the cell will produce when irradiated by photons of a particular wavelength. The *EQE* of a silicon solar cell includes the effect of optical losses such as transmission and reflection. However, it is often useful to look at the quantum efficiency of the light after the reflected and transmitted light has been lost. *IQE* refers to the efficiency with which photons that are not reflected or transmitted out of the cell can generate collectable carriers.

Figure 4 and 5 shows the *IQE* and *EQE* of back surface before and after passivation of the dye, respectively. The *IQE* and *EQE* spectra of dye molecules nanostructure showed similar shape in the wavelength range of 500 – 1200 nm relative to device without the dye. For the device with the dye layer the *IQE* increases about 19% from 24.26 % ($\lambda_{\text{peak}} = 990$ nm) to 43.19 % ($\lambda_{\text{peak}} = 975$ nm) (see Figure 4). Figure 5 shows the percentage of *EQE* and increases about 25% from 33.06 % ($\lambda_{\text{peak}} = 990$ nm) to 58.15 % ($\lambda_{\text{peak}} = 975$ nm). Based on both figures, the percentage of *IQE* and *EQE* at starting wavelength was reduced due to surface recombination. However, both *QE* has improved

gradually for rest of the wavelength as the absorption region of the DiO dye about 400 – 500 nm (BSF with dye layer). Other factors that contribute to degradation of the quantum efficiency in solar cells are due to low absorption, low field factor, high saturation current density, ineffective back surface field and high bulk recombination [19].

Light bias giving quite the large of photo carrier population that present under a light biasing charging traps and rearranging the electric field in the device [20]. High collection of photo carrier lead of quantum efficiency improved and the fact that energy transported rather than charge. The specially designed dye molecules used to absorb light efficiently and to couple the light absorption process to charge separation at the junction.

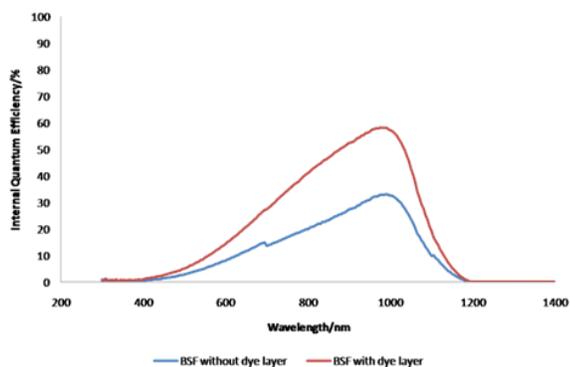


Figure 4 IQE curve of BSF with and without dye layer.

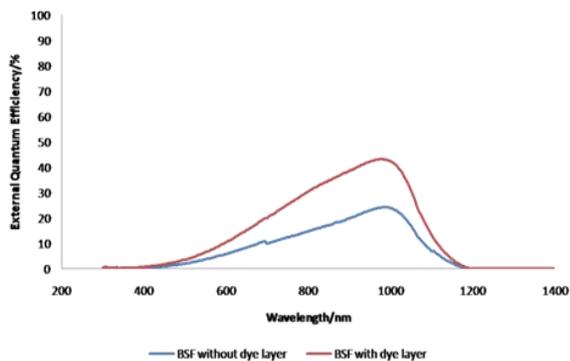


Figure 5 EQE curve of BSF with and without dye layer

4.0 CONCLUSION

We had investigated the surface modification of SiNW and BSF layers and photosensitization effect with the presence of dye molecules nanostructure via photoluminescence (PL) spectroscopy, Light Current-Voltage (LIV) and Quantum Efficiency measurements. The significant results of IV show the improvements in the J_{sc} and FF with the dye molecules nanostructure coating on the Al-BSF bifacial solar cell. The photo-generated electron on DiO dye leads to improvement on the exciton dissociation efficiency and thus to an

increase in the electrical properties. High collection of photo carrier lead of internal and external quantum efficiency improved about 19% and 25%, respectively, reasonably is due to energy transported to the junction. Therefore, it is believed that modification using photosensitization with DiO dye has improved the BSF layer performance in bifacial solar cell. Further investigation is needed to optimize this finding.

Acknowledgement

The author would like to acknowledge various financial supports from Zamalah Penyelidikan under CRIM, UKM, ERGS/1/2012/TK07/UKM/03/4, GGPM-2012-085 and GGPM-2014-048.

References

- [1] Nelson, J. 2003. *The Physics of Solar Cells*. London: Imperial College Press.
- [2] Wenham, S. R., M. A. Green, M. E. Watt, and R. Corkish. 2009. *Applied Photovoltaic*. Second Edition. UNSW: Centre for Photovoltaic Engineering.
- [3] Takato, H., Sakata, I., and Shimokawa, R. 2006. Modification of Surface Potential of Silicon by Organic Molecules. *IEEE 4th World Conference on Photovoltaic Energy Conference*. 249-252.
- [4] Aberle, A. G. 2001. Overview on SiN Surface Passivation of Crystalline Silicon Solar Cells. *Solar Energy Materials and Solar Cells*. 65 (1-4): 239-248.
- [5] Ciampi, S., Harper, J. B., and Gooding J. J. 2010. Wet Chemical Routes To The Assembly Of Organic Monolayers On Silicon Surfaces Via The Formation Of Si-C Bonds: Surface Preparation, Passivation And Functionalization. *Chemical Society Reviews*. 39: 2158-83.
- [6] Sieval, A. B., HoutBvd, Zuilhof, H., and Sudhölter, E. J. R. 2001. Molecules Modeling of Covalently Attached Alkyl Monolayers on the Hydrogen-Terminated Si(111) Surface. *Langmuir*. 17: 2172-81.
- [7] Sieval, A. B., Huisman, C. L., Schonecker, A., Schuurmans, F. M., Van Der Heide, A. S. H., Goossens, A., Sinke, W. C. Zuilhof, H., and Sudholter, E. J. R. 2003. Silicon Surface Passivation by Organic Monolayers: Minority Charge Carrier Lifetime Measurements and Kelvin Probe Investigations. *J. Phys. Chem. B*. 107(28): 6846-6852.
- [8] Choi, J-H., Roh, S-C., Jung, J-D., and Seo, H-I. 2013. Chemical HF Treatment for Rear Surface Passivation of Crystalline Silicon Solar Cells. *Transactions on Electrical and Electronic Materials*. 14: 203-7.
- [9] Angermann, H. 2002. Characterization of Wet-Chemically Treated Silicon Interfaces By Surface Photovoltage Measurements. *Anal Bioanal Chem*. 374: 676-80.
- [10] Nemanick, E. J., Hurley, P. T., Brunschwig, B. S., and Lewis, N. S. 2006. Chemical And Electrical Passivation Of Silicon (111) Surfaces Through Functionalization With Sterically Hindered Alkyl Groups. *Journal of Physical Chemistry B*. 110: 14800-8.
- [11] Danos, L., Greef, R., and Markvart, T. 2008. Efficient Fluorescence Quenching Near Crystalline Silicon from Langmuir-Blodgett Dye Films. *Thin Solid Films*. 516(20): 7251-7255.
- [12] Danos, L., and Markvart, T. 2009. Efficient Light Harvesting with LB Films for Application in Crystalline Silicon Solar Cells. *Materials Research Society Symposium Proceedings*. 1120: 1120-M01-04.
- [13] Danos, L., and Markvart, T. 2010. Excitation Energy Transfer Rate from Langmuir Blodgett (LB) Dye Monolayers to Silicon: Effect of Aggregate Formation. *Chemical Physics Letters*.

- [14] Kuhn, H. 1970. Classical Aspects of Energy Transfer in Molecules System. *The Journal of Chemical Physics*. 53(1): 101-108.
- [15] Dexter, D. L. 1979. Two Ideas on Energy Transfer Phenomena: Ion-pair Effects Involving the OH Stretching Mode, and Sensitization of Photovoltaic Cells. *Journal of Luminescence*. 18-18: 779-784
- [16] Jia, G., Steglich, M., Sill, I., and Falk, F. 2012. Core-shell Heterojunction Solar Cells on Silicon Nanowire Arrays. *Solar Energy Materials and Solar Cells*. 96: 226-230.
- [17] Canham, L. T. 1990. Silicon Quantum Wire Array Fabrication by Electrochemical and Chemical Dissolution of Wafers. *Applied Physics Letters*. 57: 1046-8.
- [18] Ee, D. T. H., Sheng, C. K., and Isa, M. I. N. 2011. Photoluminescence of Porous Silicon Prepared by Chemical Etching Method. *The Malaysian Journal of Analytical Sciences*. 15 (2): 227-231.
- [19] Sepeai, S., Sulaiman, M. Y., Sopian, K., and Zaidi, S. H. 2012. Surface Passivation Studies on n+pp+ Bifacial Solar Cell. *International Journal of Photoenergy*. Article ID 278764: 1-7.
- [20] Fonash, S. J. 2010. *Solar Cell Device Physics*. Burlington, USA: Academic Press.