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Si FUNCTIONALIZATION WITH DYE MOLECULAR AS LIGHT-HARVESTING MATERIAL

(Pemfungsian Silikon dengan Molekul Pewarna sebagai Bahan Penuaian Cahaya)

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Abstract

The surface plays an important role in thin silicon solar cells, especially with regard to the surface state and interface electronic properties that influence the electron and hole to recombine. In order to keep the recombination loss at a tolerable minimum and avoid an unacceptably large efficiency loss when moving towards thinner silicon materials, the surface must be electronically wellpassivated. Passivation is the most significant step for the functionalization of silicon. In this study, Si functionalization with a dye molecule might increase the absorption of light that acts as light-harvesting material on the silicon surface. Two types of dye molecular were used; DiL (λ_{peak} = 549 nm) and DiO (λ_{peak} = 484 nm). Both dyes were deposited using a spin-coating technique. These dye layers on the silicon surface were characterized using a Kelvin probe (KP) and photoluminescence (PL) spectroscopy. A different mechanism of slow charge trapping and detrapping was observed using KP measurement. A lifetime decay was observed that indicated a slow process of charge detrapping, owing to light trapping inside the dye/SiNW interface, with a slow process for an equilibrium to establish between the surface states and the space charge region. An average lifetime of the entire fluorescence decay process was recorded at about 1.24 ns (DiO) and 0.22 ns (DiL), using PL spectroscopy. We show conclusively that these two types of dye can be used as light absorbers, in order to improve the surface properties of the silicon.

Keywords: Si functionalization, dye molecular, light harvesting, Kelvin probe, lifetime

Abstrak

Permukaan memainkan peranan penting dalam sel-sel suria silikon nipis terutama keadaan permukaan dan ciri-ciri elektronik yang mempengaruhi elektron dan lohong untuk bergabung semula. Untuk mengekalkan kehilangan penggabungan semula itu sekurang-kurangnya boleh diterima dan mengelakkan kehilangan kecekapan apabila bergerak ke arah bahan silikon nipis, permukaan mesti secara elektronik juga dipasifkan. Pemasifan adalah langkah yang paling penting untuk pemfungsian silikon. Dalam kajian ini, pemfungsian silicon dengan molekul pewarna mungkin meningkatkan penyerapan cahaya yang bertindak sebagai bahan penuaian cahaya pada permukaan silikon. Dua jenis molekul pewarna telah digunakan; DiL (λ_{puncak} = 549 nm) dan DiO (λ_{puncak} = 484nm). Kedua-dua pewarna telah dimendapkan menggunakan teknik salutan putaran. Permukaan silikon telah dicirikan menggunakan Kelvin probe (KP) dan spektroskopi kefotopendarcahayaan (PL). Satu mekanisma yang berbeza untuk penjeratan dan penyahjeratan cas yang perlahan telah diperhatikan menggunakan pengukuran Kelvin probe. Pereputan seumur hidup diperhatikan dan menunjukkan bahawa proses penyahjeratan cas yang perlahan akibat proses memerangkap cahaya di dalam pewarna/muka SiNW yang lambat untuk keseimbangan di antara keadaan permukaan dan rantau cas ruang. Satu jangka hayat purata proses pereputan pendarfluor keseluruhan telah mencatatkan kira-kira 1.24 ns (DiO) dan 0.22 ns (DiL) menggunakan spektroskopi PL. Kami menunjukkan dengan pasti bahawa kedua-dua jenis pewarna boleh digunakan sebagai penyerap cahaya untuk memperbaiki sifat-sifat permukaan silikon.

Kata kunci: pemfungsian silikon, molekul pewarna, penuaian cahaya, Kelvin probe, jangka hayat

Introduction

The surface plays an important role in thin silicon solar cells, especially with regard tothe surface state and interface electronic properties. The properties are defined by the density and nature of the surface and interfaces states, owing to unsaturated dangling bonds. These surface states act as recombination centres for electrons and holes, which may influence the surface properties. In order to keep the recombination loss at a tolerable minimum and avoid an unacceptably large efficiency loss when moving towards thinner silicon materials, the surface must be electronically well passivated. Passivation is arguably the most important step for the functionalization of silicon. The function of passivation layer is to provide good dielectric properties, low surface recombination velocity, controlled immobile charge density and device stability at elevated temperature, under bias or operating conditions.

Silicon functionalization is a process of adding new functions, features, capabilities or properties to a material, by changing the surface chemistry of the material. This process can be performed by attaching molecules or nanoparticles to the surface of a material. The most commonly used passivation in silicon solar cells is thermally grown silicon dioxide (SiO_2). According to Aberle [1], this method is capable of providing extremely low surface states densities on high resistivity silicon. However, by using high temperature, the bulk lifetime will degrade significantly, as well as the stability of passivated surfaces. Another method has been developed on passivation layers deposited at low temperatures below 450ºC, which is silicon nitride (SiN_x) front-side passivation using plasma-enhanced chemical vapour deposition (PECVD) [1, 2].This method has proved to give an outstanding degree of electronic surface passivation with the best passivation quality obtained for silicon-rich SiN films [3]. However, several problems associated with the high silicon content of these SiN films like poor etchability, hindering the local opening of the SiN by means of chemical etching as routinely used in the fabrication of high-efficiency solar cells, and high absorption in the UV range of the sun spectrum, reducing the short-circuit current of the cell.

Over the last decade, there has been growing interest in organic monolayers attached directly to the silicon surface. Passivation with organic monolayers is shown to produce surfaces that are stable in hot solvents, acids and bases. In addition, there are number of studies on dye molecules have been carried out over thelast 30 years, resulting in the need for large quantities of high-quality material to achieve good solar cell efficiency [4]. Dexter [5] suggested that the generation of electron-hole pairs in a semiconductor via Forster resonant energy transfer (FRET) from an excited dye molecule represents an attractive prospect for solar energy conversion. A molecular layer near the semiconductor with an emission energy that exceeds the bandgap can transfer the excitation energy non-radiatively, to excite an electron from the valence band to the conduction band. The possibility of silicon sensitization via non-radiative electronic energy transfer from dye molecules on the surfacehas been proposed as a feasible approach for enhancing the photo-generation carrier rates in solar cells [6]. A common technique used for dye-molecule passivation is the Langmuir Blodgett (LB) method. This technique allows a controlled way of depositing dye monolayers. A previous study on the excitation energy transfer from LB dye monolayers to crystalline silicon substrates has been reported by Danos et al. [7]. The excitation energy of the LB dye and how it is affected by aggregate formation within the layer was investigated. Time-resolved emission spectra (TRES) and decay curves were recorded at different distances fromthe silicon surface. They found that the energy transfer rate for the monomer to silicon was double than that of the dimer to the silicon. The efficient light harvesting using dye molecules with LB films has been studied. According to Danos et al. [6], the fluorescence lifetime of the dye monolayer is shortened significantly when it presents near the silicon surface, signifying the efficient energy transfer.

Thus, this study aims to investigate the functionalization of Si with the addition of dye molecules which can improve the absorption of energy photons on the silicon surface. The usage of dye on the silicon will function as a light-harvesting material to enhance the absorption of light and improve the energy photon penetration to the bulk. A new method for deposition of the dye using spin-coating rather than the LB technique was demonstrated.The characteristics of the dye molecules were observed to explore the possibility of each dye as a light-harvesting material. Scanning Kelvin probe and photoluminescence spectroscopy were used to measure the charge-trapping mechanism and lifetime decay for each dye.

Materials and Methods

Dye molecules were fabricated on double-sided *n*-type S1 (111) wafers (float zone [FZ] quality) with 525 μm thickness, with resistivity, $\Omega = 50 – 100\ \Omega$ cm, using a spin-coating technique. Solutions NH_4OH (27%, Fluka), HCl (27%), H_2SO_4 (30%, Merck), H_2O_2 (30%, Sigma-Aldrich), HF (49%, Sigma-Aldrich), HNO_3 (70%, Merck) and chloroform (Merck) were used directly without further purification. DiO and DiL dyes were purchased from Sigma-Aldrich.

The substrates were subjected to cleaning, usinga standard Radio Corporation of America (RCA) cleaning method. Firstly, the organic impurities and the metals wereremoved from the silicon surface by wet-chemical oxidation in a solution of RCA 1 for 10 min at 70ºC. Next, the formed oxide was removed in a diluted hydrofluoric acid (HF). Secondly, the silicon wafer was soaked into a piranha solution that contained 3 parts H_2SO_4 and 1 partH_2O_2 for 15 minutes. When finished, the wafer was transferredto a container with overflowing deionized water. In the second wet-oxidation step, the wafer was dipped in a solution of RCA 2 for 10 minutes at 70ºC. Afterwards, wafers were subsequently textured using a metal-assisted chemical etching (MACE) method. Therefore, silicon nanowires (SiNW) will grow on the silicon surface. SiNW was prepared following the method described by Jia et al. [8], using a mixture of $AgNO_3$ and HF at room temperature. A mixture of $AgNO_3$ (0.02M) and HF (5M) was added to the etching cell. The etching process was stopped after 20 min and the sample was rinsed thoroughly with deionized water. Here, porous silicon hadgrown on the silicon surface, but,the surface needed to be cleaned with several steps to remove the silver dendrite on the sample surface. The cleaning procedure started with a 2 min dipping in concentrated 65% of HNO_3. After that the sample was rinsed in deionized water several times, followed by with 8 min dipping in 5% HF to remove the oxide layer on the sample surface. Hexamethyldisilazane (HMDS) was used to silylate the front surface of the wafer to make it hydrophobic. A few drops of HDMS solution were placed into the closed container and then it was leftit overnight. At the same time, the dyes of DiO and DiL were prepared by diluting themin chloroform solution, respectively. Then, the DiO or DiL were deposited on the treated wafers sample using a spin-coating method.

Surface morphology and microstructural properties of silicon nanowires (SiNW) were characterized using a field emission scanning electron microscope (FESEM) model SU8000 from the Hitachi Corporation. FESEM was performed after the formation of SiNW to investigate the cross-section image and estimate the length of nanowires with the increaseinetching time. The topographical images of the SiNW were investigated using NanosurfeasyScan 2 atomic force microscopy (AFM). The NanosurfeasyScan 2 AFM system is an atomic force microscope that can measure the topography and several other properties of a sample with nanometer resolution.The AFM output determines the surface morphology of SiNW on silicon wafer, as well as determines the surface roughness. The AFM system consists of a cantilever with a sharp tip at its end to scan the sample surface, controller and control software. When the sensor tip comes in contact with the sample, a repulsive force acts between them. The force acting on the tip can then be determined by detecting the deflection of this cantilever. Finally, the image of deflections appears on the software.The surface photovoltage (SPV) is the illumination-induced change in the surface potential.The SPV is determined by a low response of LED light using a scanning kelvin probe (SKP) with software SKP version 5.05 (KP Technology). The KP is a non-contact, non-destructive vibrating capacitor device, used to measure the work function of conducting materials, or the surface potential of a semiconductor or insulating surfaces. The KP consists of aflat circular electrode placed at the top and parallel to a stationary electrode. The gold references tip normally vibrates and has no contact with the sample. The lifetime decay for each dyes were characterized using photoluminescence spectroscopy (PL). By having the emission wavelength, the time-resolved photoluminescence graph was plotted and the average lifetime can be determined using the equation 1 below:

$$(\tau) = \frac{B_1 t_1^2 + B_2 t_2^2}{B_1 t_1 + B_2 t_2} \tag{1}$$

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.

Results and Discussion

Microstructure and Morphology

Past research by Ibrahim et al. [9] optimizes the related etching time for growing the silicon nanowires (SiNWs) on Si (111). The microstructure, morphology and topography of SiNW fabricated by a single step of themetal-assisted chemical etching(MACE) process on *n*-type Si (111), was investigated for samples subjected to different resistivity and etching time. From the observation, the shorter etching time resulted insmall pore size, low surface roughness and shorter length of nanowires [9]. In this study, SEM and AFM explored the microstructure and morphology of the SiNW. The SEM and AFM images of SiNW for 10, 20 and 40 min etching times of *n*-type Si (111) with low resistivity (50–100 Ω cm) are depicted in Figure 2. The SEM image shows the growth of SiNW on the silicon surface through MACE method. The thickness of microstructure SiNW was estimated about 317 nm (10 min), 440 nm (20 min) and 1.79 μm (40 min). Extended the etching time will produced longer length and thinner nanowires. In this experiment, the continuous experiment was done by using the shorter time and length of nanowires which is 20 min. The etching time of 20 minwas chosen because it gives more significant based on charge trapping mechanism. The typical SEM images show vertically free-standingnano wires (NWs) formed by a prolonged period of etching. A similar result was also obtained by Leontiset al. [10]. The study reported that the SiNW length was measured using SEM and transmission electron microscopy (TEM), at about 6 μm (20 min etching time) and 18 μm (60 min etching time), respectively. The SiNW length became thinner and created a large quantityof porous nanowire with increased etching time. The topography images of SiNW investigated using AFM are depicted in Figure 2. The surface roughness of SiNW was measured, which was 74.592 nm for 20 min.

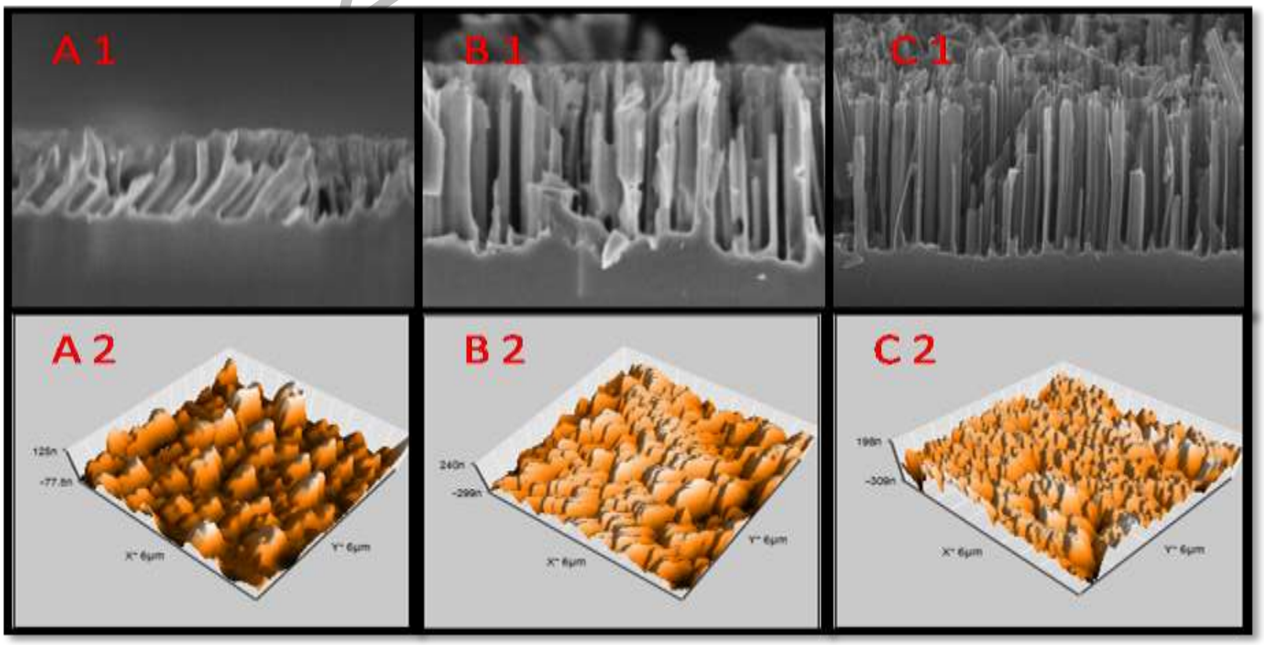

Figure 2. View of cross section on SiNWs and topography 3D images for different etching time (A) 10 min, (B) 20 min and (C) 40 min. No. 1 represent as SEM images and no. 2 denote as AFM images

Charge-trapping Mechanism

The difference mechanism of charge trapping and detrapping of charge on the silicon substrate layer was investigated by KP measurement. The surface charging was measured by continuously monitoring the position of the Fermi level of the illuminated semiconductor and measured in the dark. This investigation will provide information about SPV, as well as the decay time upon the deactivation of light. The surface photovoltage (SPV) is a well-established technique for the characterization of semiconductors, and provides both optical and transport properties of different regions in the material under study, with high sensitivity to defect states in the sample at its surface, bulk, or any buried interface [11]. As a contactless method, SPV is a standard technique for characterizing poorly understood compound semiconductors, where the fabrication of ohmic contacts or special device structures may be difficult. The SPV for native oxide, SiNW on the silicon surface, DiO layer on SiNW and DiL layer on SiNW,are depicted in Figure 3, where different patterns of the charge-trapping mechanism are observed.

For all samples, an initial time for the work function is in a dark condition. Figure 3(a) shows the SPV result for silicon native oxide. A fast drop inwork function of -20 mV is observed when the sample is illuminated from ***A*** to ***B***. The fast drop is a result of the excess electrons and holes produced by the light in the conduction and valence band that flatten the band of the semiconductor [12]. Under illumination, the bands are flattened from point ***B*** to ***C,*** which is not evidence of trapping of electrons in the surface states of silicon native oxide. When the shutter was closed at point ***C***, the work function rose up immediately to point ***D,*** which is equal in magnitude to theinitial time condition. At this point, no detrapping process took place. A similar result was obtained by Ibrahim et al. [12], suggesting this mechanism reflects a normal recombination process, owing to the recombination of excess holes and electrons in the valence and conduction bands.

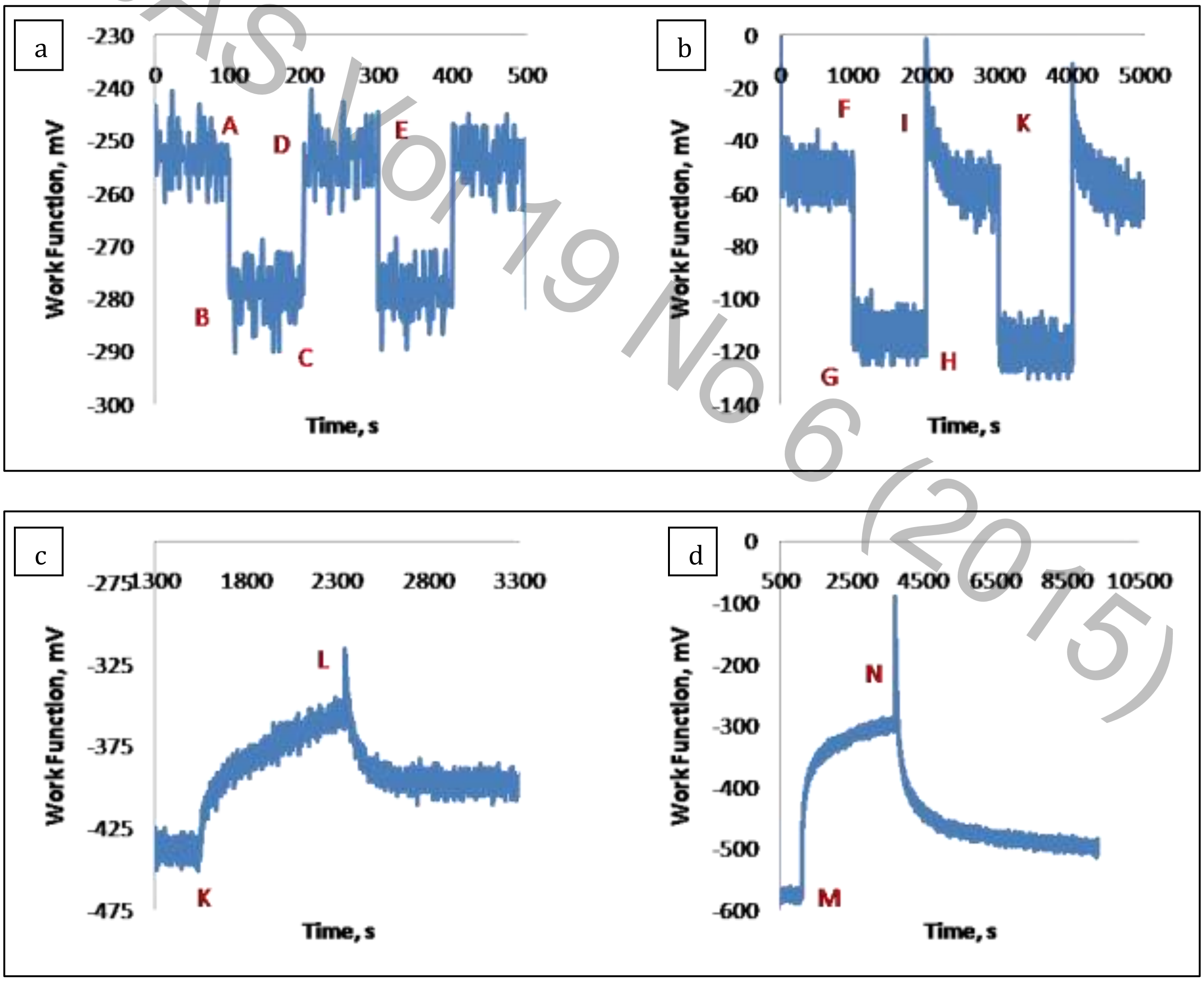

Figure 3. Changes of work function (mV) over time (s) upon illumination of sample (a) Si native oxide (b) SiNW on silicon substrate (c) DiO on SiNW (d) DiL on SiNW

A slightly different SPV pattern was observed for the SiNW sample on the silicon surface, as shown in Figure 3(b). A fast drop in work function of -40 mV is observed when the sample is illuminated (point ***F*** to ***G***). The bands flatten because of light induced in the SiNW layers. When the shutter was closed at point ***H***, the band flattening disappeared and the work function rose up immediately by about -100 mV. The signal suddenly rose and gained an optimum point of work function before it started relaxation time. Lifetime decay was observed at point ***I*** which indicated a slow process of charge detrapping taking place before it reached point***J***. This mechanism of trapping changed from a slow to a fast process, which is reflected bya normal recombination process owingto the recombination of the excess holes and electron recombination in the valence and conduction bands.

The DiO or DiL dyes were attached tothe treated SiNW layers with HMDS vapour. Figures 3(c) and (d) shows the SPV results for DiO and DiL, where the initial time of the work function is constant. Upon illumination, the SPV signal shows upward growth and increases rapidly in the first few seconds and then growth is exponential over time. At points***K*** to ***L*** and ***M*** to ***N***, the subsequent slow exponential increase in the SPV signal made the band bending larger than the baseline. The surface potential in the dyes/SiNW interface indicated a positive sign of the SPV signal. The present work suggested that some of the excess holes are captured in the dye/SiNW interface layers and made electron accumulate atthe surface. For a longer period of the illumination mode, much slower charge trapping is filled in the dyes'/SiNW interface layer. After the shutter is switched off at points***L*** and ***N***, the signal is stimulated to the optimum point before it decays, with the initial lifetime constant at (-325 mV) for DiO and (-100 mV) for DiL, respectively. At this point, the lifetime decay was observed that indicated a slow process of charge detrapping taking place, owing to the light trapping inside the dye/SiNW interface, with a slow process for equilibrium to establish between the surface states and the space charge region. Unusual charge trapping and detrapping is observed for both samples of dyes on the SiNW surface.

Photoluminescence Spectroscopy

Photoluminescence (PL) spectroscopy analysis is a powerful tool in the characterization of surfaces and interfaces. PL analysis is simple but quite versatile. Furthermore, PL is the spontaneous emission of light from a material under excitation. The excitation energy and optical intensity can be chosen to study the different regions and recombination mechanisms near interfaces [13]. However, the absorption of the incident light depends on the excitation energy. Table 1 shows the time-resolved PL result added toEq. 1 to calculate the average lifetime. As a result, the average lifetime for DiO is about 1.24 ns, while DiL is about 0.22 ns. Figure 4 shows the time-resolved PL for DiO and DiL on SiNW samples, as no peak appeared for SiNW and Si native oxide samples. An average lifetime recorded through time-resolved PL could be explained by the lifetime decay in KP measurement for both dye samples.The findings of this result suggest that the photon energy charges up and make excess carriers that are generated and trapped in the dyes'/SiNW interface layers. It demonstrates the effect of light passing through/transmitted through the charge layer as the illumination was visible in the absorption region of the DiO and DiL compounds.

Table 1. Time Resolved Photoluminescence value

Parameter	DiO	DiL
t_1(ns)	0.0658	0.0469
t_2 (ns)	1.2127	1.1792
B_1	0.749	0.936
B_2	0.006	0.007
X_2	1.446	1.126
t	1.24 ns	0.22 ns

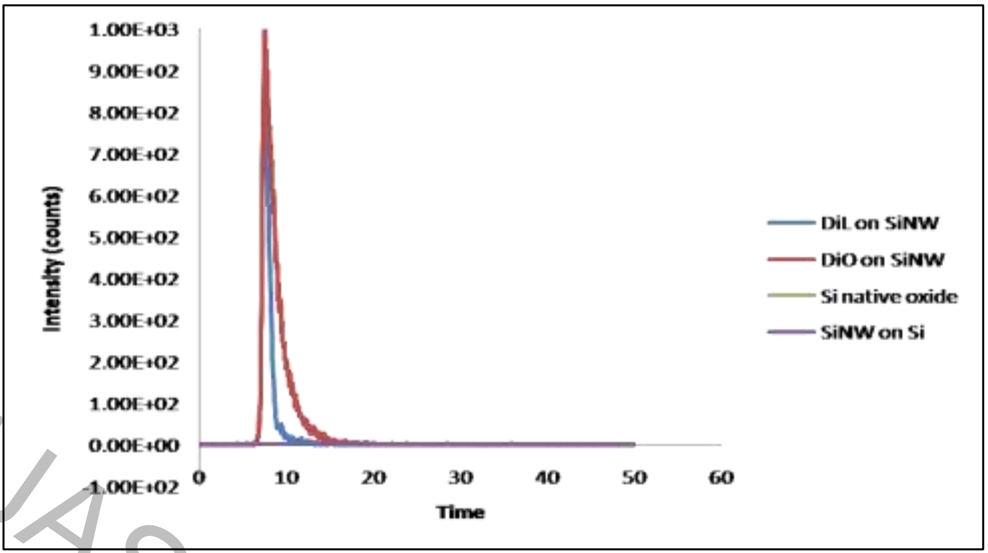

Figure 4. Time resolve photoluminescence graph for DiL and DiO on SiNW, Si native oxide and SiNW on silicon

Conclusion

The dye molecules via DiO and DiL on SiNW layers were characterized using KP and PL measurements, to explore the possibility of each dye passivatedon the silicon surface can actsas a light-harvesting material. The KP and PL used to measure the charge-trapping mechanism and lifetime decay for each dye. Further investigation on Si functionalization was explored using dye molecules as light-harvesting materials to capture more energy photons. From this study, both dyes (DiO and DiL) show asignificant effect on the charge-trapping mechanism as evidenced by KP and PLspectroscopy. For KP measurement, the charge-trapping mechanism on the dyes'/SiNW interface samples occurs during illumination, and charge detrapping take place as a slow process. Significantly, the light trapping occurs inside the dye/SiNW interface asa slow process before it reaches an equilibrium state between the surface states and the space charge region. As a result, unusual charge trapping and detrapping is observed for both samples of dyes on the SiNW surface. The lifetime decay of each dye was determined using PL, and the average lifetime for DiO was recorded at about 1.24 nsand0.22 ns for DiL. We proposed that the photon energy charges up and makes excess carriers that are generated and trapped in the dye's/SiNW interface layers. Thisdemonstrates the effect of light passing through/transmitted through the charge layer, as the illumination was visible in the absorption region of the DiO and DiL compounds. Based on these data, we show conclusively that both dyes have changed the functions, capabilities, features and properties of the silicon surface.

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