Supporting Information


The Silicon:Colloidal Quantum Dot Heterojunction

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Supplementary Information

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The c-Si:CQD diode was fabricated by spin-casting an n-type PbS CQD film on a p-type c-Si wafer. The c-Si wafer was pre-treated using tetrabutyl ammonium iodide (TBAI) before CQD deposition. The typical doping for TBAI treated PbS CQD film was on the order of $10^{17}$ cm$^{-3}$[1]. The doping concentration of the Si wafer was chosen to be $10^{17}$ cm$^{-3}$ in order to achieve ideal depletion region in the CQD film without significantly reducing the minority carrier lifetime, which is typical of highly doped silicon. Low minority carrier lifetimes result in poor saturation currents [2, 3].
Figure 1. Dark Current-Voltage (I – V) characteristics of c-Si:CQD devices. The red curve shows the I – V curve of a diode fabricated using the 2% HF treatment on the silicon surface, prior the CQD film deposition. The black curve shows the I – V of a device fabricated using the I₂ treatment for the silicon surface. The area of the samples is 0.049 cm².
Figure 2. X-Ray Photoelectron Spectroscopy of silicon wafer after 2% HF treatment. The peak at 99 eV corresponds to 2p core level of bulk Si. There is no evidence of silicon oxide at 103 eV.

Figure 3. XPS spectrum of Iodine 3d_{5/2} (dotted line) measured on the I\textsubscript{2}-treated silicon surface accompanied by a fit (continuous line). The peak position of 3d\textsubscript{5/2} is centered at 619.72 eV and it is shifted to lower binding energy compared to molecular iodine (binding energy = 620.8 [4] and 619.9 [5,6]). The error associated with the measurement is 0.01 eV.
Figure 4. EQE curves of c-Si:CQD devices treated with I$_2$. The photocurrent has been recorded at 0, 2, and 7 V reverse bias. In all the cases the spectrum doesn’t present any CQD contribution to the photocurrent in the infrared region beyond 1100 nm.

Table 1. Minority carrier lifetime of silicon wafer p-type, doped $10^{17}$ cm$^{-3}$, after surface treatment.

<table>
<thead>
<tr>
<th></th>
<th>I$_2$</th>
<th>Br$_2$</th>
<th>CH$_3$I</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier lifetime (µs)</td>
<td>28</td>
<td>19</td>
<td>27</td>
<td>15</td>
</tr>
<tr>
<td>Surface velocity (cm/s)</td>
<td>523</td>
<td>570</td>
<td>528</td>
<td>591</td>
</tr>
</tbody>
</table>

The carrier lifetime $\tau = \frac{\Delta n(t)}{G(t) \cdot \frac{d\Delta n(t)}{dt}}$, where $\Delta n(t)$ is the time dependent excess carrier density and $G(t)$ is the photogeneration rate, has been calculated from transient photoconductance decay measurements. A very short pulse of light produces an excess of minority carriers that recombine in the bulk and at the surface. The light is off during the actual measurement so $G(t) = 0$. The specified minority carrier density used to evaluate the carrier lifetime is $n = 10^{15}$ cm$^{-3}$. Surface
recombination velocity has been calculated from the relation $\frac{1}{\tau} = \frac{1}{\tau_{\text{bulk}}} + \frac{2S}{W}$ where $\tau_{\text{bulk}}$ is the carrier lifetime of p type silicon $10^{17}$ cm$^{-3}$ in doping, S is the surface recombination velocity and W is the wafer thickness.

Figure 5. Cyclic voltammetry of a 150 nm thick film of PbS CQD on a fluorinated tin oxide substrate.

Cyclic Voltammetry measurements have been done in Propylene Carbonate using Ag/Ag+ as standard electrode. Forward and reverse scans have been repeated four times at a rate of 100
mV/s, to show reversible cycles. The cathodic peak (LUMO level) is measured to be -1.07 V relative to the Ag/Ag+ electrode potential and 4.08 V relative to the vacuum level. Samples preparation and measurements have been carried out in an inert atmosphere.

**Figure 6.** Kelvin Probe Measurements (KP) measurements on surface-treated silicon wafers. Silicon wafer cleaned with 2% HF solution is used as a control. Gold, deposited on silicon wafer, is used as reference. The measurements were performed by sampling on different areas of the surface to reduce sensitivity to local variations due to surface contaminants.

I$_2$ treated samples show a relative shift of the work function at the surface towards deeper energies as evidenced by KP measurements. This is justified by the different electronegativity of silicon (X = 1.90) and iodine atoms (X = 2.66) which induces charge rearrangement at the iodine terminated silicon surface [7 – 9]. Larger relative work function measured for CH$_3$I and Br$_2$ treated samples indicates mid-gap Fermi level pinning. Variation of the work function has been combined with Fermi level shift determined from measurements of Si core level in XPS. Figure 8 shows the energy level relationships used in this analysis under various Si surface treatments. The quantities $\phi_0$ and $\phi$, in orange, represent the work function of the control and treated sample respectively. These values were measured by KP. $E_{0B,\text{core}}$ and $E_{B,\text{core}}$, in purple, represent the
binding energies of the Si core level of the control and treated sample respectively. These values were measured by XPS. \( \Delta E_F \) represents a shift of the Fermi level in the bandgap at the surface in the case of band bending. This shift takes place gradually through the depletion region in the bulk of the Si to a depth \( w \) away from the surface. \( \Delta E_{\text{vac}} \) represents a sudden shift in the vacuum level at the surface, induced by a surface dipole resulting from charge transfer between Si surface atoms and adsorbed species.

\[ \Delta E_{\text{B,core}} = E_{\text{B,core}} - E_{\text{0B,core}} = \Delta E_F \]  
\[ \Delta \phi = \phi - \phi_0 = \Delta E_{\text{vac}} - \Delta E_F \]  
\[ \Delta E_{\text{vac}} = \Delta E_F + \Delta \phi \]

**Figure 7.** Schematic of relevant energy levels for XPS and Kelvin probe analysis

The equations relating measured quantities for XPS and Kelvin probe are listed below:
We measured the Si 2p core level signal ($E_{B,\text{core}}$) of the treated silicon wafer and subtracted it from the corresponding value of our control, the H-terminated silicon wafer $E_{0B,\text{core}}$ to obtain, $\Delta E_F = E_{B,\text{core}} - E_{0B,\text{core}}$. The vacuum level offset $\Delta E_{\text{vac}}$ was evaluated according to the following equation $\Delta E_{\text{vac}} = \Delta \phi + \Delta E_F$ where $\Delta \phi = \phi - \phi_0$, $\phi$ is the work function of the modified silicon wafer and $\phi_0$ is the work function of our control. The band diagrams of halogen-treated silicon wafers determined from these measurements are shown in Figure 8.

**Figure 8**: Energy band alignment of halogen-treated p-type silicon (doping $10^{17}$ cm$^{-3}$). Band bending and vacuum level shift induced by surface dipole is reported. Flat band condition is assumed for the control (H-treated silicon).
Figure 9. Dark current-voltage characteristics of halogen and HF treated silicon wafers. The devices have been reverse biased up to 7 Volt. The area of the samples is 0.049 cm$^2$. 
**Electro-optical model**

Table 2. Physical parameters of the photodiode simulated using SCAPS software. Values of band gap, electron affinity and carrier mobility of silicon and PbS CQDs are taken from literature [1, 3, 10, 11]. Trap state density at the interface were finely tuned to match the EQE experimental results.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Silicon</th>
<th>Interface (I₂)</th>
<th>Interface (CH₃I)</th>
<th>Interface (Br₂)</th>
<th>PbS CQDs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band Gap(eV)</td>
<td>1.12</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
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<tr>
<td>Electron Affinity(eV)</td>
<td>4.05</td>
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<td>Thickness (µm)</td>
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<td>-</td>
<td>-</td>
<td>0.15</td>
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<tr>
<td>Doping(cm⁻³)</td>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>10¹⁷</td>
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<tr>
<td>e-mobility (cm²/V sec)</td>
<td>372</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>6.85 x 10⁻³</td>
</tr>
<tr>
<td>h-mobility (cm²/V sec)</td>
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<td>-</td>
<td>-</td>
<td>3.85 x 10⁻³</td>
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<tr>
<td>Diffusion length (µm)</td>
<td>360 (Lₙ)*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10⁻² (Lₚ)*</td>
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<tr>
<td>Lifetime (µs)</td>
<td>130 (τₙ)*</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10⁻² (τₚ)*</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Trap state type</th>
<th>Neutral</th>
<th>Donor</th>
<th>Acceptor</th>
<th>Acceptor</th>
<th>Donor</th>
<th>Neutral</th>
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<tbody>
<tr>
<td>Density (cm⁻³)</td>
<td>10¹¹</td>
<td>5*10¹¹(cm⁻³)</td>
<td>1*10¹²(cm⁻³)</td>
<td>2x10¹² (cm⁻³)</td>
<td>1*10¹² (cm⁻³)</td>
<td>10¹⁶</td>
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<tr>
<td>Trap energy level (eV)</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.6</td>
<td>0.2</td>
<td>0.6</td>
</tr>
<tr>
<td>Electron trap cross section (cm⁻²)</td>
<td>10⁻¹⁵</td>
<td>10⁻¹⁵</td>
<td>10⁻¹⁵</td>
<td>10⁻¹⁵</td>
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<td>10⁻¹⁵</td>
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</tr>
</tbody>
</table>

* Lₙ, τₙ are the diffusion length and carrier lifetime for electrons, Lₚ, τₚ for holes.
References


