Techno Analysis of Upconversion Technique in Solar Cell

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Abstract: - The maximum theoretical conversion efficiency is 16% for silicon-based solar cells and currently this is the material which dominates the photovoltaic cell market. Generally, solar cells on the market today do not produce much electricity from ultraviolet and infrared light (<400 nm and >1100 nm wavelengths, respectively); this light is either filtered out or absorbed by the cell, heating the cell. That heat is wasted energy, and could lead to damage to the cell. Attempt of this paper is to discuss the technology of Upconversion technique of solar spectrum by various Upconverter materials like La₂Mo₇O₂₄:YbEr, NaYF₄:Er₃⁺ and BSSC with ZnSO₄: YbEr and PbS-QDs. An upconverter cell and solar cell model is also discussed in.

Keywords:- Up-conversion, Solar Spectral Conversion, Rare earth Materials for Upconversion

I. INTRODUCTION

A. WHY UP-CONVERSION?

Sunlight in space at the top of Earth’s atmosphere at a power of 1366 watts/m² is composed (by total energy) of about 50% infrared light, 40% visible light, and 10% ultraviolet light. At ground level this decreases to about 1120–1000 watts/m², and by energy fractions to 44% visible light, 3% ultraviolet (with the Sun at the zenith, but less at other angles), and the remainder infrared. Thus, sunlight's composition at ground level, per square meter, with the sun at the zenith, is about 527 watts of infrared radiation, 445 watts of visible light, and 32 watts of ultraviolet radiation.

A single junction solar cell optimally performs under monochromatic light at wave length $\lambda_{opt}$ $\sim \frac{1240}{Eg}$ (with $\lambda_{opt}$ in nm and band gap ($E_g$) in eV). Semiconductor solar cells effectively convert photon of energy close to semiconductor gap ($E_g$) this is due to the mismatch between the incident solar spectrum and spectral absorption properties of material. The maximum theoretical conversion efficiency is 16% for silicon-based solar cells and 28% for gallium arsenide-based solar cells. Regardless of the material used, the spectral response from these solar cell depend on the depth of the p-n junction, the absorption coefficient of the fabrication materials, cell junction area exposed to sunlight and wave length of incident light. The magnitude of open-circuit voltage and short circuit current are strictly dependent on the absorption capability of the materials used in the fabrication of the solar cells.

Photons with energy $E_{ph}$ smaller than the band gap are not absorbed and their energy is not used for carrier generation. Photons with energy $E_{ph}$ larger than band gap are absorbed, but excess energy ($E_{ph} - E_g$) is lost due to thermalization of generated electrons.

Two primary losses arise from the intrinsic properties of the semiconducting absorbers: (a) sub-band gap energy photons, for which the photons’ energy is not sufficient to excite the semiconductor and (b) thermalization of charge carriers, generated by the absorption of high-energy photons with energy larger than the band gap of the solar cell. These Spectral losses associated with a single junction silicon cell can be as large as 50%. Now the only way to reduce losses is the efficient use of the solar spectrum. Wavelength of solar spectrum vary from 100nm to 1mm. Ultraviolet radiations account for 100nm to 380nm visible light comes in the range of 380nm to 700nm and infrared rays ranges from 700nm to 1mm.

There are three ways in which the cell efficiency of silicon solar cells may be improved by better exploitation of the solar spectrum down-conversion (cutting one high energy photon into two low energy photons), photoluminescence (shifting photons into wavelength regions better accepted by the solar cell) and up-conversion
(combining low energy photons to one high energy photon). Here in this paper we talk about Upconverters.

Solar cells are made with junction depths varying from .6 to .5µm and can have smooth or rough surfaces. In order to increase the short wavelength response at wavelength less than 700nm junction should be made close to surface, while in order to increase the long wavelength response at a wavelength greater than 700nm junction should be made far below the surface so varying the junction from the depth is not an effective method to minimise spectral losses.

B. WHAT IS UP-CONVERSION?

“Squeezing” of this wide solar spectrum to a single small band of spectrum without too many losses would greatly enhance solar cell conversion efficiency over 80%, which is slightly dependent on band gap. Considering the ideal band of silicon to be 2eV the optimal wavelength of the band spectrum will be

\[ \lambda_{opt} = \frac{1240}{E_g} \]

\[ = \frac{1240}{2} \]

\[ = 620 \text{ nm} \]

That is the visible light region in the solar spectrum so squeezing the solar spectrum to the range of visible light is going to improve the conversion efficiency of the solar cell. Let us focus on the infrared region of the spectrum since it accounts for around 50% of the total incident radiation on the earth surface.

II. PARAMETRIC REQUIREMENTS FOR OPTIMUM PERFORMANCE OF SOLAR CELL DEVICES

The solar cell performance is strictly dependent on short-circuit current in the device junction and is a function of wavelength (λ), absorption coefficient (α), Diffusion constant (D) and diffusion length (L) in the p and n regions. The expression for short-circuit current can be written as

\[ J_{sc} = \lambda / 1 - 1 / a \ln \left[ e^{-D / \lambda} - e^{-D / a} \right] \]

If we notice the wavelength versus absorption coefficient graph for Silicon we can notice that As wavelength increases absorption coefficient reduces. For 500nm its around \(10^4 \text{ cm}^{-1}\) and for 1100nm its around \(10 \text{ cm}^{-1}\).

III. PRINCIPAL OF UPCONVERSION TECHNIQUE

Up converters modify the spectrum of photons that are not absorbed by the solar cell to effectively shift the Infrared spectrum region to the visible spectrum; black reflectors usually are applied well.

Energy of the Photon \(E_{ph} = \frac{h \nu}{\lambda} \) where \(h \) is planks constant, \(\nu\) is speed of light and \(\lambda\) is wavelength. So the infrared spectrum which is having high wave length is going to have less energy since energy of the photon is inversely proportional to wavelength.

![Upconverter](image)

Figure 1

Figure 1 explains that two or more incoming photons react with the up-converter, which emits at least one photon with higher energy than the incoming photons.

Energy transfer of upconverter mechanism is the most efficient; it involves energy transfer from an exited ion named sensitizer (Ytterbium,Yb3+) to a neighbouring ion named activator (Erbium, Er3+) Fig.2. Upconverter usually combine an active ion, of which energy level schemes is employed for absorption and a host material, in which the active ion is embedded. The most efficient upconversion has been reported for lanthanide ion couples (Yb,Er) and (Yb,Tm).

Rare earth complexes (Yb,Er,Tm,Ho) with high quantum efficiencies absorb light at shorter wavelengths and subsequently emit light at longer wavelengths. The high energy region of the solar light spectrum is shifted to longer wavelengths; hence the cell output power is expected to become higher because the emitted light can match with the higher sensitivity region in longer wavelengths of a basic solar cell.
There are several common mechanisms for UC. The simplest mechanism, which is denoted ground state absorption/ excited state absorption (GSA/ESA), is schematically depicted in Fig. 2. Photon absorption leads to the generation of an excited state inside a luminescent centre via two sequential absorption processes (dotted arrows in Fig. 3) involving a real meta-stable intermediate state (or, more generally, intermediate band). If the generated excited state relaxes via a radiative transition (vertical solid arrow in Fig. 3), then an up-converted photon with higher energy is emitted. In a second, very efficient UC-mechanism the energy required for the emission of an up-converted photon is sequentially transferred to the luminescent centre by nearby ions, which absorb the low energy photons, a process that is called energy transfer upconversion (ETU). The ions thus act as sensitizers or antennas for the luminescent centre. In a combination of the previous processes the luminescent centre is first excited into the intermediate state via GSA. Another excited luminescent centre then transfers energy to the initially excited centre, to lift it into a higher excited state (a process denoted GSA/ETU) [2].

For application to silicon solar cells the properties that will ultimately determine the benefit of the process include [3]:

- Absorption range higher than 1100 nm (E < 1.12 eV);
- Emission lower than 1100 nm;
- Low excitation intensity (range of W=cm²);
- High up-conversion efficiency and
- High transmittance of the up-converted light.

IV. SYSTEM MODEL

Viorel Badescu et al [4] explain a model of cell and upconverter system. Three types of transitions occur inside the converter: a band-to-band transition (associated to electron–hole pair recombination) and two intermediate transitions between the bottom edge of the conduction band (CB) and the intermediate level and between the intermediate level and top edge of the valence band (VB), respectively. These two intermediate transitions are associated to electron–hole pair generation. These three types of transitions may be seen as three independent two-band systems with individual electrochemical potential and the whole up-converter may be represented in an equivalent circuit by three fictitious cells connected in series (Fig. 4). The cell C2 corresponds to the band-to-band transition, with electrochemical potential difference $\mu_{C2}$. Devices C3 and C4, which correspond to the two intermediate transitions, can be modelled as cells with electrochemical potential difference $\mu_{C3}$ and $\mu_{C4}$, respectively. Finally, C1 in Fig.4 represents the real solar cell, with electrochemical potential difference $\mu_{C1}$.
Cell C2 (of band gap $E_u = E_g$) can emit and absorb photons in the energy range $(E_u, E_u+E_2)$. Cells C3 and C4 emit and absorb low-energy photons in well-defined energy intervals (corresponding to transitions through intermediary level). This way, a photon of energy $E_1 < E_u$ hits an electron in the valence band that climb on the intermediary level.

A second photon of energy $E_2 < E_u$ transfers its energy to it and the electron reaches the conduction band. After the recombination of this electron, a photon of energy $E > E_g$ may be emitted and absorbed by the solar cell C1. Cells C2, C3 and C4 are connected in series.

V. EXPERIMENTAL DATA ON UPCONVERTER MATERIALS

It has been well known that up-conversion of phosphorus emit photons with a higher energy. This process is based on the presence of at least two metastable exited states that are used to add up energy of excitation photons, which convert IR or near IR to visible luminance.

A. $La_2Mo_2O_9$: YbEr

$La_2Mo_2O_9$: YbEr is a Upconverter. Spectral conversion photovoltaic cells consisting of $La_2Mo_2O_9$: YbEr phosphor coated silicon wafers which converts photons in to electricity with efficiency depend on the wavelength, were fabricated using screen printing technique. This UC phosphor is coated on the rear side of PV cell with a translucent film with 1mm in thickness was formed.

Yen-Chi Chen et al [5] conducted experiments on $La_2Mo_2O_9$: YbR ($R = Er, Ho$) and came up with the following results $La_2Mo_2O_9$: YbEr with 980nm laser excitation could emit a yellow–green light at observed emission peaking at 525nm, 550nm and 655nm respectively. A comparison of the spectra indicates that phosphor coated silicon surface can reduce reflection and enhance light absorption.

Table 1 Comparison of $I_{sc}$, $V_{oc}$, and $\eta$ (±0.01%) for bare and UC $La_2Mo_2O_9$:Yb,R ($R = Er, Ho$) Phosphor-coated solar cells (No. 1, $La_2Mo_2O_9$:Yb,Ho; No. 2 and 3, $La_2Mo_2O_9$: Yb,Er; No. 4, $La_2Mo_2O_9$:Yb,Er coated on the rear surface of the Si cell)*

<table>
<thead>
<tr>
<th>No.</th>
<th>$I_{sc}$ Bare (A)</th>
<th>$I_{sc}$ Coated (A)</th>
<th>$\Delta I_{sc}$ (A)</th>
<th>$\eta$ Bare (%)</th>
<th>$\eta$ Coated (%)</th>
<th>$\Delta \eta$ Increase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.05</td>
<td>8.18</td>
<td>0.13</td>
<td>16.53</td>
<td>16.78</td>
<td>0.25(+1.50%)</td>
</tr>
<tr>
<td>2</td>
<td>8.04</td>
<td>8.19</td>
<td>0.15</td>
<td>16.52</td>
<td>16.81</td>
<td>0.29(+1.76%)</td>
</tr>
<tr>
<td>3</td>
<td>8.06</td>
<td>8.21</td>
<td>0.15</td>
<td>16.53</td>
<td>16.80</td>
<td>0.27(+1.63%)</td>
</tr>
<tr>
<td>4</td>
<td>8.13</td>
<td>8.31</td>
<td>0.18</td>
<td>16.23</td>
<td>16.67</td>
<td>0.44(+1.27%)</td>
</tr>
</tbody>
</table>

The UC phosphor coating on Si cell devise could increase the $I_{sc}$ & efficiency by increment in visible light input as shown in Table 1. From this we can also conclude UC material coated on rear side of the cell provides better results.

Figure 5 Reflection Vs Wavelength

Up conversion phosphors coated on the surface of a single crystalline silicon solar cell
could effectively increase the photovoltaic Isc, Voc, and conversion efficiency. The increase in conversion efficiency was about <3%, which was mainly attributed to the low up conversion efficiency of the existing up-converters whose performance was limited by both the absorption range and conversion efficiency.

They have also reported a drastic reduction in reflectance (Fig.5) after coating La2Mo2O9: YbEr on the rear side of the solar cell. Therefore, the UC phosphor was found to reduce light scattering and increase light input. The UC phosphor coating on a Si cell device could increase Jsc and efficiency by increasing the visible light input.

B. NaYF4:Er3+

Shalav et al. (2005) [6] have demonstrated a 2.5% increase of external Quantum efficiency due to upconversion using NaYF4:20% Er3+. Trupke, T et al [7] in 2006 conducted experiments with NaYF4:Er3+ have reported a high quantum efficiency for the spectral range from 1480nm to 1580nm wavelengths for a bifacial buried contact silicon solar cell with the NaYF4: 20% Er3+-phosphor attached to the rear surface. Also they have reported a considerable reduction in reflection of the IR wavelength spectrum so there is a considerable increase in absorption efficiency.

De Wild et al. [8] in 2011 have demonstrated upconversion for a-Si cells with NaYF4 co-doped with (Er3+, Yb3+) as upconverter. The upconverter shows absorption of 980 nm (by the Yb3+ ion) leading to efficient emission of 653 nm (red) and 520-540 nm (green) light (by the Er3+) after a two-step energy transfer process. The narrow absorption band around 980 nm for Yb3+ limits the spectral range of the IR that can be used for up conversion.

An external quantum efficiency of 0.02% at 980 nm laser irradiation was obtained. By using a third ion (for example Ti3+) as a sensitizer the full spectral range between 700 and 980 nm can be efficiently absorbed and converted to red and green light by the Yb-Er couple. The resulting light emission in the green and red region is very well absorbed by the cell with very good quantum efficiency for electron-hole generation.

C. Yb/Er-DOPED PHOSPHOR WITH PbS- QUANTUM DOT

As far we have discussed the conversion efficiency of solar cell were able to be increased only up to less than 3% which is mainly due to the less absorption capability of UC. A.C. Pan et al in 2010 suggested to improve this absorption capacity of UC by introducing semiconductor nanocrystals called Quantum Dots (QD). Lead sulphide (PbS) is one of a kind Quantum Dot. These QDs have large quantum efficiency and high indices of refraction compared to the phosphors, which Si devices can take advantage of. The energy transfer will probably occur through radiative emission from the QDs followed by absorption by the UC phosphor.

EQE for the solar cell is significant in the range 350–1100 nm, the UC layer is able to extend it (although with a very low response) in the 1488–1564 nm range. The PbS QDs have absorption precisely in the range where neither the Bifacial Silicon Solar Cell (BSSC) itself nor the UC take advantage of the light (1200–1500 nm), and the emission takes place in the range where the UC is active. Thus A.C. Pan et al demonstrated that the combination of an Yb/Er-doped phosphor with PbS-QDs enhances the UC performance [9]. The improvement in photocurrent detected for a BSSC with ZnSO4: YbEr and PbS-QDs is in all cases 60% better than without them, demonstrating the beneficial effects of the QDs embedded in oxide or silicone, which increases the coupling of the light to the Er atoms [9].

VI. CONCLUSION

We have seen that use of upconverter will aid in enhancing the photocurrent and there by considerable increase in conversion efficiency is possible. A considerable reduction in reflection of the IR wavelength spectrum so there is a considerable increase in absorption efficiency is also possible. Using La2Mo2O9: YbEr has given a conversion efficiency of almost 3%. Experiments with NaYF4:Er3+ gave EQE close to 2.5%. Use of Quantum dots can help in overcoming the low absorption capabilities of UC’s and there by a much better conversion and EQE can be achieved. Theoretically solar cells without UC can reach efficiency of 30% and with UC an efficiency of 37.4% and here we have seen practically that an efficiency increase of 3% was possible with UC and with the combination of Quantum dots it still has been increased. Research is still going on in this field for much better results.
References


