Indoor photovoltaics with Perovskite solar cells and nanostructured surfaces

Nathalie Carrier
Abstract

This work is a contribution to the development of a high efficiency photovoltaic cell adapted to indoor environment.

Indoor light has been defined and a power of approximately 0.8 mW has been calculated to be available for harvesting, allowing the supply of low power sensors.

A CH$_3$NH$_3$PbI$_3$ Perovskite simulation has shown that this Perovskite has a quantum efficiency close to 1 over visible range using a hole transport material. It stands for good candidate to replace conventional a-Si as indoor light harvester.

Finally nanostructured films have been investigated in order to improve diffuse light harvesting. The deposition of a Polystyrene beads monolayer on top of the cell front surface has been performed. Experiments and simulations have shown resonances. More studies are needed to conclude on the enhancement this nanostructuration can provide.

Acknowledgement

Firstly I would like to thank Jean-Claude Bourgoint, director at Green ITN at Orange Labs and Stephane Le Masson, head of Research for Energy and Environment Department at Orange Labs for welcoming me as a trainee.

My thanks also go to Dr. Thomas Rivera, Research project manager at Orange Labs Networks, who supervised and mentored my work, for his attention, and for all the time he awarded to me.

I would like to thank Dr. Christian Tanguy, Researcher at Orange Labs Networks, for sharing with me a piece of his knowledge about refractive indices analytical models.

I would like to thank every person I have worked with within these few months, among them: Pr. Serge Ravaine, Pr. Thierry Toupane, Christian Bourliatand, Emeline Beaudri, Jose Parra-Diaz.

Finally, I would like to thank Pr David Haviland, my KTH supervisor, who helped me realizing that work and who gave me all his attention.
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<td>AR</td>
<td>Anti-reflection</td>
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<td>BG</td>
<td>Band gap</td>
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<td>EQE</td>
<td>External Quantum efficiency</td>
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<td>FDTD</td>
<td>Finite difference time domain</td>
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<td>IoT</td>
<td>Internet of things</td>
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<td>IPV</td>
<td>Indoor photovoltaics</td>
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<td>PC</td>
<td>Photonic crystal</td>
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<td>PCE</td>
<td>Power conversion efficiency</td>
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<td>PS</td>
<td>Polystyrene</td>
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<td>QE</td>
<td>Quantum efficiency</td>
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<td>QFL</td>
<td>Quasi-Fermi level</td>
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Chapter 1

Introduction

1.1 Background

The Internet of Things (IoT) is a physical objects network. These objects collect and exchange data thanks to embedded network connectivity. Experts estimate that IoT will connect no less than 50 billion objects by 2020.

Expected-life time for such devices must match with standard life-times of radio systems, about 10-15 years. Supplying power to these objects must be solved, as batteries will not last this long. Maintenance costs are an issue and batteries replacement is expensive for Telecom. Orange is working on self-fed energy solutions. Several physical effects (thermoelectricity effect, piezoelectric effect...) could be implemented but the most suitable one seems to be photovoltaic (PV) powersupply. For home IoT networks (temperature sensors, motion sensors, ect.), a specific PV solution is required.

Unlike solar illumination, indoor light is limited in spectral range, spanning only the visible, and often emanating from diffuse and disturbed sources of low intensity. LEDs are expected to dominate indoor lighting in the following years. Consequently LED spectrum is considered. PV technology needs to be adapted to such environment.

Since 1976, Amorphous Silicon (a-Si) has been dominating the indoor photovoltaic (IPV) market as it is cheap to manufacture, has 10 years life-time and it reacts well under weak intensity. a-Si has already been commercialized to supply small devices like calculators. However its power conversion efficiency in the laboratory has not exceed 13.4% (See Figure 1.1) and commercial cells have not exceeded 6 to 8% \[1\]. Moreover their efficiency decreases by 10 to 20% in the 6 first months of use due to the Staebler–Wronski effect \[2\]. This
study focus on Perovskite based photo voltaic materials, a new material to replace a-Si.

**Perovskite as the new a-Si**

Aside from the predominant development of silicon-based solar cells, organic solar cells have been developing and particularly Pervoskite-based solar cells have recently stood out with the most rapid growth in efficiency in the PV history (See Figure 1.1).

These organic Perovskite (PVK) solar cells are based on materials from the perovskite family. In only one year of study a 15% Power Conversion Efficiency has been certified [3] and a proven efficiency of 20% has recently been confirmed by NREL (See Figure 1.1).

PVK have a strong absorption below their band gap (\(\alpha \approx 10^5 \text{ cm}^{-1}\)) at 550 nm, which is ten times crystalline Silicon (c-Si) absorption), and the latter is adapted to visible (cutoff wavelength at around 800 nm) so they are suited for indoor and thin film applications. Moreover, PVK are easy, fast and cheap to manufacture (five time cheaper than Silicon [5]). They stand out as promising candidates for large-scale production and widespread applications.

**Nanostructuring for higher efficiency**

A photonic crystal (PC) is a periodic structure with a pitch of order one hundred nanometers that affects the propagation of photons, as an ionic lattice affects electrons propagation in solids. PCs have emerged since 1987 with Yablonovich’s first article [6].

PCs can contribute to enhance PV efficiency. For example, nanostructured surfaces have already been placed on a-Si solar cells [7] from a collaboration between the Nanotechnologies Institute of Lyon (INL) and Orange. A complementary study has shown that LED spectra are absorbed up to 90% thanks to the nanostructured surface [8]. Nanostructured PVK based solar cells are promising too.

The challenge with PC is that 1: they need to be made precisely enough to prevent scattering losses and 2: a robust and cheap manufacturing process needs to be designed. Orange is working with the CRPP french laboratory[9] which knows how to create photonic devices easily, at low cost, in short time and with a reproducible bottom-up approach. This so-called "Inverse Opal" technique could be transferred to large scale mass production. Inverse Opal

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1 below in terms of wavelenght or above in terms of energy.
2 CRPP: Centre de Recherche Paul Pascal, Bordeaux I
1.2 OBJECTIVES

process consists of the deposition of Polystyrene or Silica beads followed by an infiltration step and with subsequent removal of the beads.

This study focuses on a nanostructured device able to increase the acceptance angle of a solar cell, or in other words, adapted to diffuse illumination (in contrast to solar beams). Another way nanostructuring could enhance PV performance would be by increasing the optical path inside the active material.

1.2 Objectives

On the one hand PVK is a good absorbent and well adapted to weak illumination in the visible range. On the other hand, nanostructuration can enhance photovoltaics performance by increasing the cell’s acceptance cone.

The goals of this study is to give a first understanding of Perovskite photovoltaics matched to indoor environment. A first planar structure is studied and later on the objective is to see how simple nanostructuring improves angular collection. The simple nanostructuring studied is a monolayer of Polystyrene (PS) beads deposited on top of a planar cell.

1.3 Methodology

The LED spectrum is first studied. Similar to the 33% limit for solar irradiance, a calculation of the best gap energy is performed. A planar cell is designed and studied by a classic analytical method: the Matrix Transfer Method. Its Quantum Efficiency (QE) is simulated and compared with a-Si QE.

Finally the contribution of nanostructuring is studied. First of all, the numerical Finite Difference Time Domain method is introduced. A monolayer of PS beads deposited on a glass substrate is experimentally characterized and numerically simulated with FDTD method. A discussion about the possibility of enhancement is proposed.
CHAPTER 1. INTRODUCTION

Figure 1.1: NREL Best Research-Cell Efficiencies.
Chapter 2

Towards optimal indoor PV

In this part a study of indoor environment is proposed. More precisely, the maximum conversion efficiency expected from a LED spectrum is derived, similar to the famous Shockley-Queisser limit on the maximum possible efficiency of solar cells which states that p-n junctions solar cells are limited to around 30% efficiency \[9\]. Later on this limit has been revised to around 33% at 1.4 eV.

In this section the calculation of the optimized gap is adapted to the LED spectrum. The Mathematica code is inspired by code from Steve Byrnes \[10\].

2.1 Ideal band gap calculation

From the irradiance spectrum \(I_r\) between \(\lambda_{min}\) and \(\lambda_{max}\) (expressed in \(W.m^{-2}.nm^{-1}\)), the number of photons per unit time, per unit energy-range, per unit area can be expressed as:

\[
N_{\text{photons}} = \frac{\lambda}{E^2} \times I_r \left[ \frac{1}{s \: m^2 \: J} \right]
\]  

(1)

The total number of photons with energy above the band gap is obtained from the integral of \(N_{\text{photons}}\) from \(E_g\) to \(E_{max}\).

\[
N_{E>E_g} = \int_{E_g}^{E_{max}} N_{\text{photons}}(E) \, dE
\]  

(2)

Some of these photons do not lead to the creation of an electron-hole pair due to recombination processes. For a direct band gap junction recombination happens predominantly through radiative recombination. Like Shockley
and Queisser’s first calculations [9], only radiative recombinations are considered, proportional to the product of the electron and hole density, \( n \) and \( p \) respectively;

\[
R \propto np \quad (3)
\]

Electron density in a junction is related to electrons Quasi-Fermi level (QFL), and hole density is related to holes QFL. In order to derive the radiative recombination rate \( (R_{rad}) \), the case when electrons and holes QFLs are equal is first detailed and then extended to the case when QFLs split.

**No QFL splitting**

This configuration is equivalent to a solar cell at zero bias in the dark, under thermal equilibrium. The semiconductor is assumed to behave like a perfect blackbody above the band gap (BG) and to be transparent below, the radiative recombination rate is expressed:

\[
R_{rad0}(E_g) = \frac{2\pi}{c^2 h^3} \int_{E_g}^{E_{max}} \frac{E^2}{\exp\left(\frac{E}{k_B T_{cell}}\right) - 1} \, dE \quad (4)
\]

**QFL splitting**

When the electron QFL moves by \( E_1 \) towards the conduction band, the new electron concentration is expressed as:

\[
n' = n \times \exp\left(\frac{-E_1}{k_B T_{cell}}\right) \quad (5)
\]

Similarly when the holes QFL moves by \( E_2 \) towards the valence band:

\[
p' = p \times \exp\left(\frac{E_2}{k_B T_{cell}}\right) \quad (6)
\]

To sum up \( np \propto \exp\left(\frac{E}{k_B T_{cell}}\right) \) with \( E \) the total QFL splitting. In the best possible case, the QFL splitting is equal to the external voltage (it can be larger) leading to:

\[
R_{rad}(E_g, V) = R_{rad0}(E_g) \times \exp\left(\frac{eV}{k_B T_{cell}}\right) \quad (7)
\]

\[
= \frac{2\pi}{c^2 h^3} \exp\left(\frac{eV}{k_B T_{cell}}\right) \int_{E_g}^{E_{max}} \frac{E^2}{\exp\left(\frac{E}{k_B T_{cell}}\right) - 1} \, dE
\]
2.2. VALIDATION ON SOLAR SPECTRUM

The above expression is simplified according to Wurfel and Ruppel’s calculation \[11\]. They conclude that it would be more accurate to use:

\[
\frac{2\pi}{c^2 h^3} \int_{E_g}^{E_{\text{max}}} \frac{E^2}{\exp \left( \frac{E-\epsilon V}{k_B T_{\text{cell}}} \right) - 1} \, dE
\]  

(8)

but the difference is negligible for gaps above 200 meV.

The current density can be expressed as the electric charge times the number of photons above the band gap which to not recombine:

\[
J(V, E_g) = e \times (N_{E>E_g}(E_g) - R_{\text{rad}}(E_g, V))
\]  

(9)

The short circuit current is simply expressed as the current density at zero voltage:

\[
J_{sc}(E_g) = J(0, E_g)
\]  

(10)

The open-circuit voltage is obtained solving \(J(V, E_g) = 0\):

\[
V_{oc} = \frac{k_B T_{cell}}{e} \times \log \frac{N_{E>E_g}(E_g)}{R_{\text{rad0}}(E_g)}
\]  

(11)

The maximum power point on the I-V curve defined by \(V_{mp}\) and \(J_{mp}\) can be find solving:

\[
\frac{d}{dE} (V \times J(V, E_g)) = 0
\]  

(12)

Finally the maximum efficiency as a function of band gap is derived:

\[
\eta_{\text{max}}(E_g) = \frac{P_{\text{out}}^{\text{max}}}{P_{\text{in}}} = \frac{V_{mp} J_{mp}}{P_{\text{in}}}
\]  

(13)

\(P_{\text{in}}\) is calculated from the irradiance data as:

\[
P_{\text{in}} = \int_{E_{\text{min}}}^{E_{\text{max}}} E \times N_{\text{photons}} \, dE
\]  

(14)

2.2 Validation on solar spectrum

The solar spectrum (AM1.5G) is taken from the NREL data base available online \[12\] and represented on Figure 2.1. The integral of the curve is 1000 W.m\(^{-2}\).

A Mathematica code added in Appendix A solves Equation 12 using Equation 9 and the maximal efficiency as a function of BG is derived from Equation 13. The maximum efficiency curve for solar spectrum as a function of
Figure 2.1: AM1.5G solar spectral irradiance.

Figure 2.2: Solar maximum efficiency curve.

BG is plotted in Figure 2.2. The calculated ideal band gap is located around
2.3 APPLICATION TO LED SPECTRUM

1.35 eV and corresponds to a 33.5% power conversion efficiency (PCE) which is consistent with the 33% limit.

In Figure 2.3 the integral over the solar spectra for energy higher than $E$ is plotted on the same graph as the maximum efficiency curve. The integral starts to decrease as approximately the ideal band gap energy.

![Normalized solar spectrum and comparison](image)

**Figure 2.3:** Normalized solar spectrum (black) and comparison between maximum efficiency curve (red) and the integral for $E > E_g$ of normalized solar irradiance (blue).

2.3 Application to LED spectrum

As no normalized LED spectra exists, the LED spectrum used for calculation has been measured from a 3 Watt white LED module (Model-ILL3A0001 from CML Innovative Technologies). To measure the spectrum an integrating sphere and a spectro-photometer (HR4000 model from Ocean Optics) have been used. The irradiance intensity is not standard and the maximum efficiency depends on a competition between the number of incident photons
above the BG and the recombination rate. The maximum efficiency value will depend on the incoming intensity, however the maximum location (in eV) will remain the same.

In order to have a good estimation of the maximum efficiency for typical usage, a LED spot available on the market is studied (model MR16 GU10 6W SHARP from ADDIS Lighting company). This spot is composed of 2 LEDs and results in a 20° light cone as represented on Figure 2.4. According to the data-sheet, the illumination is of 900 lux 1 meter away from the spot. The latter quantity has to be converted as follow:

\[ P = \frac{E}{\eta} \left[ \frac{W}{m^2} \right] \]  

With \( P \) the power, \( \eta \) the luminous efficacy in lumens per Watt and \( E \) the illuminance in lux (lm/m²). With a luminous efficacy of 40 lm/W, it leads to a power of:

\[ P = \frac{900}{40} = 22.5 \, W/m^2 \]  

The ideal indoor band gap calculation is performed for this use case power value, meaning that the integral over the visible range is set equal to 22.5 \( W/m^2 \). LED spectrum is compared to solar spectrum in Figure 2.5. It is narrower and has a two peaks centered in 449 nm and 540 nm (equivalent to 2.77 eV and 2.28 eV respectively). This specific spectrum shape is expected to be identified in the maximum efficiency curve. The latter is plotted on
2.3. APPLICATION TO LED SPECTRUM

Figure 2.5: Solar and LED spectra in arbitrary units.

Figure 2.6: LED maximum efficiency curve.

The calculated ideal band gap is approximated to 1.9 eV with a maximum PCE of almost 60%. This is twice as much the maximum PCE for
The shape of the maximum efficiency curve as a function of energy gap is related to the two peaks spectral shape. Here again the ideal gap is located on the edge where the integral starts to decrease (See Figure 2.7).

![Normalized LED spectrum and comparison](image)

**Figure 2.7:** Normalized LED spectrum (black) and comparison between maximum efficiency curve (red) and the integral for $E > E_g$ of normalized LED irradiance (blue).

The previous calculations lead to an efficiency of 57% at 1.9 eV band gap 1 meter from the LED spot. The power received by a sensor located around a light source will depend on the angle between both. Indeed, even for an ideal emitting source (angularly uniform), the so-called Lambertian source, a $\cos\theta$ factor is involved. LEDs sources are more complex than thermal sources, and a specific correction factor should be used.

The simple case is studied of a sensor of 1 cm$^2$ surface located 1 meter away from the LED and facing the central emitting direction of the LED. As calculated before, the power received 1 meter from the spot is 22.5 W/m$^2$. Consequently, the sensor receives 2.25 mW, in the best possible case 57% are converted into electricity: 1.28 mW.

Small sensors like temperature sensors need voltage of at least 5 V and consume around 60 $\mu$A which leads to a needed power of 0.3 mW. This sensor may not be placed 1 meter away from a LED and may not face the central emitting direction of the LED like in the ideal calculation. However it
probably receives light from several light sources (2 or more LEDs and outside sun light through windows). We conclude that supplying indoor small sensors with photovoltaic effect is possible.
Chapter 3

Design of a planar Perovskites-based photovoltaics device

In this chapter, indoor PV cell design is investigated. We examine Perovskites as the active layer. The complete planar device is considered.

3.1 Introduction to Perovskites

History

High efficiency dye-sensitized solar cell (DSSCs) also called Grätzel cells were developed by M. Grätzel & B. O’Regan in 1991 at EPFL in Switzerland [13]. This organic thin film cell consists of a photo-electrochemical system and a mesoporous architecture.

In parallel, PVK was studied by D. Mitzi at IBM for LEDs applications (green emission) [14]. At that time PVK was not considered for solar applications because of stability issues and Lead toxicity.

More than ten years later, in 2009, Miyasaka et al [15] incorporated PVK in DSSCs with a liquid electrolyte. They reached 3.8% PCE but the cell was very unstable, the liquid electrolyte dissolved away the Perovskite crystallinity within a few minutes.

The stability problem was solved in 2012 by H. Snaith and M. Lee from Oxford University. They stated that PVK are stable when used with a solid hole-transport material so-called Spiro-OMeTAD. Since then the architecture of PVK based solar cells was based on Grätzel cells’s mesoporous structure.
In 2014 H. Snaith et al deleted the mesoporous structure and introduce planar structures with a PCE above 10% [10]. Nowadays, both structures exist. They are drawn in Figure 3.1.

![Figure 3.1: Perovskite cell structures: planar structure without scaffold and mesoporous structure with scaffold.](image)

Research on this topic is going on and most recently, 20% PCE cell has been confirmed by NREL (See Figure 1.1).

**Structure**

The term "Pervoskites" designates a family of materials with the same crystal structure. This ideal structure is derived from calcium titanium oxide (CaTiO$_3$) discovered in 1839 and named after the Russian mineralogist Lev Perovski. It is characterized by the general cubic structure $\text{ABX}_3$ (See Figure 3.2).

- $\text{X}$ is a halogen anion and forms an octahedral grid linked at their corners.
- At the center $\text{B}$ is a cation occupying a 6-fold coordination site.
- Between octahedra, $\text{A}$ is a cation occupying a 12-fold coordination site.

The Perovskite family is large. $\text{X}$, $\text{B}$ and $\text{A}$ can be atoms or different chemical compounds. For instance $\text{X}$ is a halogen or a mix of halogen compounds like I$_2$Cl, I$_{3-2x}$Br$_x$, or I$_{3-2x}$Cl$_x$. $\text{B}$ is any divalent metal which satisfies the charge balancing like Cu$^{2+}$, Ni$^{2+}$, Sn$^{2+}$... $\text{A}$ can be NH$_4^+$, CH$_3$NH$_3^+$, NH$_3$OH$^+$... The two cations, $\text{A}$ and $\text{B}$ have very different sizes.
CHAPTER 3. DESIGN OF A PLANAR PEROVSKITES-BASED PHOTOVOLTAICS DEVICE

Technology and processes

Manufacturing processes are important to consider. Indeed the cell has to be low-cost. Fortunately, Perovskites can be simple and cheap to produce depending on the process used, especially CH$_3$NH$_3$PbI$_3$. Four general methods to prepare this active layer exist: One-Step Precursor Deposition (OSPD), Sequential Deposition Method (SDM), Dual-Source Vapor Deposition (DSVD) or Vapor-Assisted Solution Process (VASP).

Liquid-phase processes are simpler, faster and cheaper for mass production, but water always remains and may dissolve Perovskite and decreases PCE. Evaporation processes are more expensive and more difficult to obtain but no water remains and the crystallinity is maintained.

Light harvesting properties

The major advantage of Perovskites for PV is its huge absorption. Its absorption coefficient $\alpha$ exceeds $10^5$ cm$^{-1}$ over a wide range of wavelengths (which is ten times c-Si absorption coefficient). Consequently only a small amount of material is needed. Thanks to flexibility, Perovskites are suitable for thin film solar cells.

Another advantage is that despite their organic composition, Perovskites behave like semiconductors and not like organic materials [17]. Once a photon is absorbed by the material, the electron-hole pair separates itself without any secondary process (unlike in organic solar cells). More precisely, Perovskites behave like a direct band-gap semiconductors whose gap is even tunable. As an example, mixing I with Br in Formamidinium Lead Iodide (CH(NH$_2$)$_2$PbI$_y$Br$_{3y}$) tunes the gap between 1.48 and 2.23 eV [18] as shown in Figure 3.3.
3.1. INTRODUCTION TO PEROVSKITES

Another important property is that electron and hole diffusion lengths are equal and large, around 100 nm for CH$_3$NH$_3$PbI$_3$ and as large as 1 $\mu$m [19] for CH$_3$NH$_3$PbI$_{3-x}$Cl$_x$.

However most PV adapted Perovskites are Lead-based and therefore toxic.

An other issue is that Perovskites exhibit thermal instability. In our application thermal instability is not a problem since indoor temperature is rather stable (20 degrees) and always below 40 degrees, and in this range of temperature Perovskites are stable.

Perovskite choice

The Perovskite material studied is the Methylammonium Lead Iodide: CH$_3$NH$_3$PbI$_3$ where X is I$^-$, B is CH$_3$NH$_3^+$ and A is Pb$^{2+}$. The motivation for choosing CH$_3$NH$_3$PbI$_3$ is that it composed of abundant elements, easy to fabricate and it has already been well studied (i.e. electrons and holes diffusion lengths are known as well as its band structure). Through a future collaboration between Orange and the French laboratory ISM[1] CH$_3$NH$_3$PbI$_3$ samples would be provided by the sequential deposition method at ISM. The process is low cost and reproducible (easy, cheap, fast).

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1ISM: Institut des Sciences Moléculaires, Bordeaux I
CHAPTER 3. DESIGN OF A PLANAR PEROVSKITES-BASED PHOTOVOLTAICS DEVICE

In the remainder of this thesis, PVK refers to CH$_3$NH$_3$PbI$_3$.

3.2 Photovoltaic cell design

The complete cell structure is designed. A planar structure is chosen for simplicity. A classic planar PVK solar cell is composed of a Transparent Conductive Oxide (TCO), an electron transport material, a light harvester (PVK) and a back contact. The photons enter the cell from the TCO side.

One has chosen to use ITO as TCO, TiO$_2$ as electron transport material, CH$_3$NH$_3$PbI$_3$ as light absorber and Silver as back contact (cheaper than gold).

The perovskite/TiO$_2$ interface behaves like a n-p hetero-junction with TiO$_2$ as n-doped side and perovskite as p-doped side. The cell dimensions are chosen from the literature [20] and showed in Figure 3.4.

Figure 3.4: Planar structure design.

3.3 Optical characterization

The absorption coefficients of the cell components are given in Figure 3.5. In the visible range, the absorption is mainly dominated by PVK.

The optical study of the planar cell is performed analytically using the transfer matrix method to describe the field propagation in a stratified media [23]. Each layer is characterized by its thickness and its refractive index $\tilde{n} = n' + in''$ with $n'$ the real part and $n''$ the imaginary part (also called attenuation coefficient). $n''$ is related to the medium absorption:

$$\alpha = \frac{4\pi n''}{\lambda}$$

Thanks to a Mathematica code added in Appendix B, one calculates the reflection and transmission spectra of the planar structure.
3.3. OPTICAL CHARACTERIZATION

Figure 3.5: Absorption coefficient ($\alpha$) for ITO, TiO$_2$ and PVK in visible range. Data extracted from: PVK: [4], TiO$_2$: [21] ITO: [22]. The LED spectrum is plotted as a reminder.

The code gives the calculation of the absorption of the entire cell for both S and P polarizations (Figure 3.6 and Figure 3.7). The absorption being defined as follow:

$$A = 1 - T - R$$

(1)

As R is polarization dependent, so is A.

The following chapter discusses the photon to electron conversion efficiency of the designed cell.
CHAPTER 3. DESIGN OF A PLANAR PEROVSKITES-BASED PHOTOVOLTAICS DEVICE

Figure 3.6: Planar cell absorption in P polarization.

Figure 3.7: Planar cell absorption in S polarization.
Chapter 4

Planar cell quantum efficiency

The previous cell structure can be improved by adding a hole transport material (HTM). The generated photocurrent inside two structures are investigated: a TiO$_2$/PVK junction and a TiO$_2$/PVK/HTM junction. According to the literature, the first junction is treated as a n-p junction \cite{24}, the other one is treated as a n-i-p junction \cite{25}.

4.1 Heterojunction QE calculation

Device structure

In order to simulate the external quantum efficiency (EQE) in Perovskite-based solar cells, the homojunction study developed by Sze \cite{26} has been adapted. A parallelepipedic hetero-junction composed of 2 semi conductors is considered (see Figure 4.1). The left one ($0 < x < x_j + W_1$) is n-doped, the other ($x_j + W_2 < x < H$) is p-doped. $W_1$ and $W_2$ are n-side and p-side depletion regions respectively. $H$ is the total width of the junction and $H'$ is set as $H' = H - x_j - W_1 - W_2$.

The following assumptions are considered:

1. The parallelepiped is homogeneous in the Y and Z directions.
2. The junction is abrupt and doping is constant on each side.
3. There is no electric field outside the depletion region.
4. The low-injection condition is valid meaning that the difference in charge carriers density is insignificant compared to the thermodynamic equilibrium charge carriers density.
CHAPTER 4. PLANAR CELL QUANTUM EFFICIENCY

Figure 4.1: Structure of the p-n heterojunction.

Notations

The mathematical notation used in the calculation is defined in Table 4.1 and Table 4.2

<table>
<thead>
<tr>
<th>Index : i</th>
<th>Specifies</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n-doped layer</td>
</tr>
<tr>
<td>2</td>
<td>p-doped layer</td>
</tr>
<tr>
<td>1p</td>
<td>holes in n-doped layer</td>
</tr>
<tr>
<td>2n</td>
<td>electrons in p-doped layer</td>
</tr>
</tbody>
</table>

Table 4.1: Indexes definition for QE calculation.

Spectral response calculation

Neglecting internal reflexion, the electron-hole pair generation rate as a function of position $x$ in the device is,

For $0 < x < x_j + W_1$:

$$G_1(\lambda, x) = \alpha_1(\lambda)\Phi(\lambda)[1 - R(\lambda)]e^{-\alpha_1(\lambda)x}$$  \hspace{1cm} (1a)

For $x_j + W_1 < x < H$:

$$G_2(\lambda, x) = \alpha_2(\lambda)\Phi(\lambda)[1 - R(\lambda)]e^{-\alpha_1(\lambda)(x_j + W_1)}e^{-\alpha_2(\lambda)(x-(x_j+W_1))}$$  \hspace{1cm} (1b)

An equal generation rate for electrons and holes is assumed. Under the assumption of low-injection, the one-dimensional steady-state continuity equations for minority carriers becomes
### 4.1. HETEROJUNCTION QE CALCULATION

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$G_i$</td>
<td>Electron generation rate</td>
<td>cm$^{-3}$.$s^{-1}$</td>
</tr>
<tr>
<td>$n_i$</td>
<td>Electron concentration in i-type semiconductor</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$p_i$</td>
<td>Holes concentration in i-type semiconductor</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$n_{i0}$</td>
<td>$n_i$ at thermodynamic equilibrium</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$p_{i0}$</td>
<td>$p_i$ at thermodynamic equilibrium</td>
<td>cm$^{-3}$</td>
</tr>
<tr>
<td>$\tau_i$</td>
<td>Carrier lifetime</td>
<td>s</td>
</tr>
<tr>
<td>$J_i$</td>
<td>Current density</td>
<td>A.cm$^{-2}$</td>
</tr>
<tr>
<td>$q$</td>
<td>Unit electronic charge, absolute value</td>
<td>C</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>Wavelength</td>
<td>cm</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>Optical absorption coefficient</td>
<td>cm$^{-1}$</td>
</tr>
<tr>
<td>$R$</td>
<td>Light reflection (in energy) on the first interface</td>
<td>--</td>
</tr>
<tr>
<td>$T$</td>
<td>Transmission of light in energy</td>
<td>--</td>
</tr>
<tr>
<td>$\mu_i$</td>
<td>Drift mobility</td>
<td>cm$^2$.V$^{-1}$.s$^{-1}$</td>
</tr>
<tr>
<td>$D_i$</td>
<td>Diffusion coefficient</td>
<td>cm$^2$.s$^{-1}$</td>
</tr>
<tr>
<td>$L_i$</td>
<td>Diffusion length</td>
<td>cm</td>
</tr>
<tr>
<td>$E$</td>
<td>Electric field</td>
<td>V.cm$^{-1}$</td>
</tr>
<tr>
<td>$S_i$</td>
<td>Surface recombination velocity</td>
<td>cm.s$^{-1}$</td>
</tr>
</tbody>
</table>

Table 4.2: Notations.

For holes in the n-side ($0 < x < x_j$):

$$G - \left(\frac{p_n - p_{n0}}{\tau_{1p}}\right) + \frac{1}{q} \frac{dJ_{1p}}{dx} = 0 \quad (2a)$$

For electrons in the p-side ($x_j + W_1 + W_2 < x < H$):

$$G - \left(\frac{n_p - n_{p0}}{\tau_{2n}}\right) + \frac{1}{q} \frac{dJ_{2n}}{dx} = 0 \quad (2b)$$

The current on each side consists of a drift contribution and a diffusion contribution:

$$J_{1p} = q\mu_pp_nE + qD_p\frac{dp_n}{dx} \quad (3a)$$

$$J_{2n} = q\mu_nn_pE + qD_n\frac{dn_p}{dx} \quad (3b)$$
N-side photocurrent: For the n-side of the junction, Equation 1b, Equation 2b and Equation 3b yield to:

\[ D_{1p} \frac{d^2 p_{2n}}{dx^2} + \alpha_1 \Phi (1 - R) e^{-\alpha_1 x} - \frac{p_n - p_{n0}}{\tau_{1p}} = 0 \]  

(4)

Introducing the diffusion length \( L_{1p} = \sqrt{D_{1p} \tau_{1p}} \), the general solution to the system is:

\[ p_n - p_{n0} = C_2 \cosh \left( \frac{x}{L_{1p}} \right) + C_3 \sinh \left( \frac{x}{L_{1p}} \right) - \frac{\alpha_1 \Phi (1 - R) \tau_{1p}}{\alpha_1^2 L_{1p}^2} \]  

(5)

\( C_2 \) and \( C_3 \) are determined using the boundary conditions:

- At the surface \((x = 0)\), the surface recombination is \( S_p \)
- At the depletion edge \((x = x_j)\), the excess carrier density is small due to the electric field in the depletion region

The N-side photocurrent is derived using Equation 5 and Equation 3b evaluated at the depletion edge:

\[ (J_{1p})_{x_j} = -q D_{1p} \left( \frac{dp_n}{dx} \right)_{x_j} \]  

(6)

\[ = q \Phi (1 - R) \alpha_1 L_{1p} \frac{S_{1p} L_{1p}}{D_{1p}} \times \left\{ \frac{e^{-\alpha_1 x_j} (S_{1p} L_{1p}) - (S_{1p} L_{1p}) \cosh \left( \frac{x_j}{L_{1p}} \right) + \sinh \left( \frac{x_j}{L_{1p}} \right)}{S_{1p} L_{1p} \sinh \left( \frac{x_j}{L_{1p}} \right) + \cosh \left( \frac{x_j}{L_{1p}} \right) - \alpha_1 L_{1p} e^{-\alpha_1 x_j}} - \alpha_1 L_{1p} e^{-\alpha_1 x_j} \right\} \]

\((J_{1p})_{x_j}\) is the n-side contribution to photocurrent.

P-side photocurrent: Similar calculations can be done for \( J_n \) in the right p-side using Equation 1b, Equation 2a and Equation 3a and the boundary conditions:

- At \( x = H \), the surface recombination is \( S_n \).
- At \( x = x_j + W1 + W2 \), the excess carrier density is small.
4.1. HETEROJUNCTION QE CALCULATION

\[(J_{2n})_{x_j+W_1+W_2} = -qD_{2n} \left( \frac{dn_p}{dx} \right)_{x_j+W_1+W_2} \tag{7}\]

\[\frac{q\Phi(1-R)\alpha_2 L_{2n}}{\alpha_2^2 L_{2n}^2 - 1} e^{-\alpha_2 W_2 - \alpha_1(x_j+W_1)} \times \]

\[\alpha_2 L_{2n} - \frac{S_{2n} L_{2n}}{D_{2n}}(\cosh(\frac{H}{L_{2n}} - e^{-\alpha_2 H})) + \sinh(\frac{H}{L_{2n}} - e^{-\alpha_2 H}) + \alpha_2 L_{2n} e^{-\alpha_2 H} \]

\((J_{2n})_{x_j+W_1+W_2}\) is the p-side contribution to photocurrent.

**Depletion region photo-current:** In the depletion region the carrier life time is considered to be infinite, assuming no recombination process. We still consider that there is no electric field at the depletion edge, then the photogenerated photo-current is given by:

\[J_{DR} = q \int_{x_j}^{x_j+W_1} G_1(\lambda, x) \, dx + q \int_{x_j+W_1}^{x_j+W_1+W_2} G_2(\lambda, x) \, dx \tag{8}\]

\[= q\Phi(1-R) \left[ e^{-\alpha_1 x_j} (1 - e^{-\alpha_1 W_1}) + e^{-\alpha_1(x_j+W_1)}(e^{-\alpha_2 W_2} - 1) \right] \]

**Quantum efficiency** The spectral response is obtained by summing the contribution from each of the three regions:

\[QE_1 = \frac{(J_{1p})_{x_j}}{q\Phi(1-R)} \tag{9}\]

\[QE_2 = \frac{(J_{2n})_{x_j+W_1+W_2}}{q\Phi(1-R)} \tag{10}\]

\[QE_{DR1,2} = \frac{(J_{DR})}{q\Phi(1-R)} \tag{11}\]

Finally only the design parameters and the physical parameters: \(\alpha_i, L_i, D_i\) and \(S_i\) are needed to obtain the QE of a p-n heterojunction.
CHAPTER 4. PLANAR CELL QUANTUM EFFICIENCY

4.2 N-P heterojunction structure

Device structure

Next to a n-type semiconductor PVK behaves like a p-type semiconductor. The TiO$_2$/CH$_3$NH$_3$PbI$_3$ interface is then considered as a heterojunction with TiO$_2$ n-doped and CH$_3$NH$_3$PbI$_3$ p-doped. Figure 4.2 gives the band structure of such a heterojunction.

![Figure 4.2](image)

The study of the depletion region has already been performed and a depletion region width of about 45 nm [24] (10 nm on p-side and 35 nm on n-side) has been shown.

We suggest an analytical model for the QE response of a TiO$_2$/CH$_3$NH$_3$PbI$_3$ heterojunction, using a device structure shown in Figure 4.3.

![Figure 4.3](image)

Design parameters from the previous chapter are used and physical parameters are taken from the literature [20], except for $S_{1p}$ and $S_{2n}$ which are set equal to $1 \times 10^8$ cm.s$^{-1}$. We summarize the parameters in Table 4.3.
4.2. N-P HETEROJUNCTION STRUCTURE

<table>
<thead>
<tr>
<th>Parameter</th>
<th>value</th>
<th>Unit</th>
<th>Parameter</th>
<th>value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>0</td>
<td>–</td>
<td>$L_{1p}$</td>
<td>$110 \times 10^{-9}$</td>
<td>m</td>
</tr>
<tr>
<td>$x_j$</td>
<td>$(41 - 35) \times 10^{-9}$</td>
<td>m</td>
<td>$D_{1p}$</td>
<td>0.011</td>
<td>cm$^2$.s$^{-1}$</td>
</tr>
<tr>
<td>$H_f$</td>
<td>$492 \times 10^{-9}$</td>
<td>m</td>
<td>$D_{2n}$</td>
<td>0.017</td>
<td>cm$^2$.s$^{-1}$</td>
</tr>
<tr>
<td>$W_1$</td>
<td>$35 \times 10^{-9}$</td>
<td>m</td>
<td>$S_{1p}$</td>
<td>$1 \times 10^{8}$</td>
<td>cm.s$^{-1}$</td>
</tr>
<tr>
<td>$W_2$</td>
<td>$10 \times 10^{-9}$</td>
<td>m</td>
<td>$S_{2n}$</td>
<td>$1 \times 10^{8}$</td>
<td>cm.s$^{-1}$</td>
</tr>
</tbody>
</table>

Table 4.3: Parameters for n-p junction.

Results

Using absorption spectra of the device components (see Figure 3.5), a Mathematica code calculates and plots the quantum efficiency of a TiO$_2$/CH$_3$NH$_3$PbI$_3$ p-n junction.

![Figure 4.4: Total spectral response of TiO$_2$/CH$_3$NH$_3$PbI$_3$ n-p heterojunction.](image)

In Figure 4.4, one can see the cutoff-wavelength at around 760 nm from the Perovskite and the global shape of the curve shows that the absorption of PVK dominates.

In order to better understand the role of each parameter, the Manipulate Mathematica function is used to observe the influence of each parameter. The three contributions (N-region, P-region and depletion region) to the spectral response are plotted. A screen shot of the program is given in Figure 4.5.
TiO₂ absorbs at high energy (gap = 3.2eV), its small contribution to the total spectral response located at low wavelengths ($\lambda < 350$ nm). CH₃NH₃PbI₃ absorbs in the visible range until 760 nm. It contributes for all wavelength below the cutoff wavelength. The three contributions show that most of the electron-hole generation takes place in p-doped Perovskite region. Due to the small depth of the depletion region in PVK, only small wavelengths are ab-
sorbed (corresponding to high $\alpha$). Expanding $W_2$ leads to higher depletion region contribution.

The ratio of the diffusion length to device dimension influences the QE. Both electron and hole diffusion lengths would preferably be larger than the distance to the contacts.

### 4.3 N-I-P heterojunction structure

In order to enhance the cell performance, it is possible to add a hole transport material to the cell. The structure TiO$_2$/CH$_3$NH$_3$PbI$_3$/HTM then behaves like a p-i-n hetero-junction. The QE simulation of a TiO$_2$/CH$_3$NH$_3$PbI$_3$/-SpiroOmeTAD is studied using previous calculation.

According to literature, PVK adopts the properties showed in Figure 4.6 where a part of the PVK is dominated by drift and a part by diffusion [25].

![Diagram](image)

**Figure 4.6:** TiO$_2$/CH$_3$NH$_3$PbI$_3$/SpiroOmeTAD band structure [27].

For QE calculation, one considers the n-TiO$_2$/i-CH$_3$NH$_3$PbI$_3$/p-CH$_3$NH$_3$PbI$_3$ junction. TiO$_2$ is n-doped and CH$_3$NH$_3$PbI$_3$ is separated in two regions: the drifting (i-CH$_3$NH$_3$PbI$_3$) and the diffusion regions (p-CH$_3$NH$_3$PbI$_3$) (See Figure 4.7). In the calculation the hole transport material is indirectly taken into account since Perovskite behavior is related to HTM presence.

#### Device structure

The previous discussion leads us to consider the n-p junction between TiO$_2$ and CH$_3$NH$_3$PbI$_3$ with different physical parameters (see Table 4.4). Again $S_{1p}$ and $S_{2n}$ are set equal to $1 \times 10^8$ cm.s$^{-1}$. 
CHAPTER 4. PLANAR CELL QUANTUM EFFICIENCY

Figure 4.7: TiO$_2$/CH$_3$NH$_3$PbI$_3$/SpiroOmeTAD n-i-p heterojunction.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>value</th>
<th>Unit</th>
<th>Parameter</th>
<th>value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R$</td>
<td>0</td>
<td>–</td>
<td>$L_{1p}$</td>
<td>$110 \times 10^{-9}$</td>
<td>m</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>$L_{2n}$</td>
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<td>m</td>
</tr>
<tr>
<td>$x_j$</td>
<td>$(41 - 35) \times 10^{-9}$</td>
<td>m</td>
<td>$D_{1p}$</td>
<td>0.011</td>
<td>cm$^2$.s$^{-1}$</td>
</tr>
<tr>
<td>$H'$</td>
<td>$492 \times 10^{-9}$</td>
<td>m</td>
<td>$D_{2n}$</td>
<td>0.017</td>
<td>cm$^2$.s$^{-1}$</td>
</tr>
<tr>
<td>$W_1$</td>
<td>$35 \times 10^{-9}$</td>
<td>m</td>
<td>$S_{1p}$</td>
<td>$1 \times 10^8$</td>
<td>cm.s$^{-1}$</td>
</tr>
<tr>
<td>$W_2$</td>
<td>$300 \times 10^{-9}$</td>
<td>m</td>
<td>$S_{2n}$</td>
<td>$1 \times 10^8$</td>
<td>cm.s$^{-1}$</td>
</tr>
</tbody>
</table>

Table 4.4: Parameters for the n-i-p junction.

Results

The final QE curve is given in Figure 4.8 and compared to a-SI:H QE data extracted from [27]. A screen shot of the *Manipulate* Mathematica function is shown in Figure 4.9.

In this configuration, the size of the depletion zone is large compared to the depletion zone for the p-n junction. This increase in size is responsible for the huge increase in QE.

Indeed, in the depletion region, the electron-hole pair separates and electrons and holes are driven thanks to electric field. As shown in Figure 4.9 adding HTM leads to a significant enhancement in QE. The a-Si:H external QE is plotted for comparison [27]. Unlike the simulated QE, this external QE includes the cell reflection which reduces the overall cell efficiency.

The study of the TiO$_2$/CH$_3$NH$_3$PbI$_3$ side of the total n-i-p heterojunction gives positive predictions about the cell photon to electron conversion. We conclude that the presence of the hole transport layer modifies perovskite behavior and leads to an interesting enhancement of QE.
4.3. N-I-P HETEROJUNCTION STRUCTURE

Figure 4.8: QE of both PVK-based cells compared with a-Si:H external QE [29].
Figure 4.9: Screen shot of Mathematica program for QE calculation of n-i-p structure: TiO$_2$/CH$_3$NH$_3$PbI$_3$/SpiroOmeTAD.
Chapter 5

Photonic crystal towards higher performances

In the following chapter, a photonic crystal structure to enhance the acceptance angle of the cell is studied.

5.1 Introduction to photonic crystals

A photonic crystal is a periodic dielectric structure which affects the propagation of different optical frequencies. Several types of photonic crystals exist [28]: 1D, 2D and 3D, as shown on Figure 5.1.

![Illustration of one, two and three dimensional photonic crystal](image)

Figure 5.1: Illustration of one, two and three dimensional photonic crystal [29].

The PC imposes periodic conditions for light wave propagation like the ionic lattice for electron propagation. In Figure 5.1, the different colors repre-
CHAPTER 5. PHOTONIC CRYSTAL TOWARDS HIGHER PERFORMANCES

sent different dielectric constants and the periodicity along one, two or three directions define the type of PC. The photon propagation inside the crystal are determined by the lattice geometry and index contrast.

5.2 Photonic crystal choice

Motivation

A monolayer of polystyrene beads deposited on top of a silicon solar cell has already been investigated [29] and an increase in external quantum efficiency at 800 nm by 13% has been showed. The two-dimensional PC structure had 450 nm period and is shown in Figure 5.2. Adding a single monolayer on top of a solar cell is a fast and low cost process.

![Figure 5.2: Nanospheres deposited on top of Si solar cell [30].](image)

In an optimal configuration, PS beads are deposited on top of the ITO surface. For simplicity, and due to time constraints, the PS beads monolayer has been deposited on top of a glass substrate instead of ITO, and their diameter is of 562 nm. The spread in diameter is unknown.

In the visible range indices are around $n = 1.60$ for PS, $n = 1.00$ for air, $n = 1.52$ for glass and $n = 1.90$ for ITO. The air/PS/ITO combination has a progressive index structure, whereas the air/PS/glass does not. Although an anti-reflexion coating effect is expected for PS beads on top of ITO, it is not expected for PS on glass.

In any case, the aim is to see how the nanostructured layer influences the behavior with angle, as illustrated in Figure 5.3.

---

1 Antireflexion coating effect: enhancement of transmission through a surface.
Sample fabrication

The sample has been made at the french laboratory CRPP. It consists of a single layer of PS beads deposited on top of a glass substrate. The bottom-up Langmuir–Blodgett method was used. PS beads were spread onto a water surface by using a tilted glass slide (to facilitate the process) and surfactant. The self-assembled mono-layer was transferred onto the glass substrate by first immersing the substrate completely in water, then positioning it under the mono-layer and carefully lifting them up onto the substrate. This process is the first step of inverse opal fabrication.

The PS bead array is hexagonal close packed with period equal to the bead diameter, 562 nm. The periodicity of the array is verified by the change in color of the sample with angle as shown in Figure 5.5.
CHAPTER 5. PHOTONIC CRYSTAL TOWARDS HIGER PERFORMANCES

Figure 5.5: Change in color of the nanostructured sample with angle.

Figure 5.6: Set-up experiment.

The apparatus shown in Figure 5.6 is used to characterize the sample. Three lenses are used to focus the incident beam on the sample and a Glan Thompson polarizer (anti-reflexion coating for 350-700 nm) selects either S or P polarization. A diaphragm is used to reduce the beam size on the sample and a camera is used to observe the beam impact on the sample. The rotating platform is composed of two rotary stages. The first one allows to modify the incidence
angle on the sample and the second one allows the detector to turn around the sample and collect the reflected or transmitted beam. Due to constraints with the size of the detector, angles smaller than $\theta_{\text{min}} = 20^\circ$ can not be measured.

5.4 Finite Difference Time Domain method

OptiFDTD numerical software (from Optiwave company) is used in order to simulate experimental results and to simulate PS beads on top of ITO. Simulator is numerical. Indeed, analytical model does not exist for 2D and 3D nanostructured materials.

The FDTD directly solves the time dependent Maxwell’s curl equations. The calculation can be performed on 2D or 3D meshes. Calculations are slow, so it is convenient to reduce the domain as much as possible. Boundary conditions are defined: anisotropic perfectly matched layers boundary conditions are applied on the edge of the computational window in the propagation direction and periodic conditions are used in the nanostructured plane to reduce the domain to a single unit cell. Figure 5.7 shows the defined pattern.

In order to perform a simulation, an input plane has to be defined to set the spectral range of calculation. Many designs and shapes can be created with OptiFDTD but the important point is to correctly define the media indices. OptiFDTD allows for different media but they must be well described by a Sellmeier model or a modified Lorentz-Drude model. The modeled materials and their optical properties are detailed in Appendix C.

5.5 Experimental results and comparison with simulations

The measured transmission of the nanostructured surface is plotted for both polarizations (See Figure 5.8 and Figure 5.9). The curves have been smoothed to observe the general behavior. Global transmission decreases with angle for both polarizations and local resonances are observed.

In order to validate the use of OptiFDTD software, the simulation of the transmission in P polarization at $0^\circ$ is done. The comparison between experiment and simulation is given on Figure 5.10. Comparing both curves, one can see that resonances at around 500 nm, 600 nm and 680 nm are present in both curves. However the general slope of the curves does not exactly match. There are several reasons for this discrepancy. The bead diameter is assumed to be 562 nm but this quantity has some experimental uncertainty. The diameter is assumed to be the same for all deposited beads but in reality there is
CHAPTER 5. PHOTONIC CRYSTAL TOWARDS HIGHER PERFORMANCES

Figure 5.7: Definition of the domain of calculation.

The unit cell is represented in black. Thanks to symmetry of the unit cell, periodic boundary conditions are set on the edge of the XY domain defined by the red square.

...some distribution of unknown width. This spread in diameter means that the array will not be perfectly periodic. There may also be some cracking during fabrication process. Finally some measurement uncertainties may affect the measured curves.

The use of OptiFDTD software having been validated with experiment, the simulation is extended to the very case of a PS beads monolayer deposited on top of ITO. As ITO is the entrance surface, the monolayer is expected to guide light through ITO. Transmission specta are interesting since they represent the amount of light transmitted to the active layer. The aim being to transfer as much light as possible from the front surface to the active layer (PVK). Both cases represented on Figure 5.11 are simulated.
5.5. EXPERIMENTAL RESULTS AND COMPARISON WITH SIMULATIONS

Figure 5.8: Transmission of nanostructured sample for P polarization.

Figure 5.9: Transmission of nanostructured sample for S polarization.
CHAPTER 5. PHOTONIC CRYSTAL TOWARDS HIGHER PERFORMANCES

Figure 5.10: Comparison between FDTD simulation and experiment.

Figure 5.11: Planar and nanostructured front film of the cell.

The simulated curves are plotted for P polarization in Figure 5.12 where the LED spectrum is added. We see that the resonances are not as strong as the glass sample, and their location does not seem to vary with angle. These differences can be explained by the change in index contrast. It would be nice to validate this behavior with experimental characterization. We also see that
5.5. EXPERIMENTAL RESULTS AND COMPARISON WITH SIMULATIONS

Figure 5.12: Transmission spectra (P polarization) of planar vs nanostructured sample with angle.

due to these resonances, better transmission is obtained at around 600 and 800 nm. It would be interesting to make the resonances deeper and to make them match with the two LED peaks.

A solution to strengthen resonances would be to increase the number of beads layers as shown in the PhD thesis of Hanbin Zheng [31]. This solution is more complex and takes more time to fabricate.

Changing the beads size and/or the array period can change the resonance location. Further studies are needed to relate the resonances location with the parameters of the nanostructuration.
Chapter 6

Conclusion and perspectives

This work makes three contributions to the development of high efficiency Perovskites-based photovoltaic cell 'adapted to indoor environment'. An estimate of how much power can be harvested from LED illumination is given and the conclusion is that it is enough to supply low power sensors. A study of PVK shows that it has a quantum efficiency close to 1 over visible range when using a hole transport material. Moreover its low cost of production makes it well adapted to IoT applications. Finally, a study of nanostructuring the surface of a solar cell has been done. The deposition of a Polystyrene bead monolayer on top of the front surface does not seem to enhance the transmission through the front surface. Further studies are needed to understand how the nanostructured array affects the photon motion and solar cell efficiency.
Bibliography


[8] C.E. Brès. Etude optique de cellules photovoltaïques nanostructurées (cristaux photoniques 2d) à base de a-si :h optimisées pour l’alimentation


Appendix A

Ideal bad gap calculation code

The calculation is based on the same calculation made for solar spectrum. A units package available at http://sjbyrnes.com/UnitsPackageSource.nb is called. As input user has to load a LED spectrum with two columns. Column 1 contains wavelengths in nm and column 2 contains associated irradiance.

(* Load Units Package *)
Get[UnitsPackage file path]

(* Load Irradiance spectrum and set temperature *)
Tcell = 300 kelvin;
IrLED = Import["filepath"];

(* Spectrum interpolation from \([\Lambda]\) Min to \([\Lambda]\) Max *)
LED = ({[#[1]] nm, #[2] watt/meter/meter/nm} &)/@IrLED;
LMin = 400 nm;
LMax = 800 nm;
Emin = hPlanck SpeedOfLight/LMax;
Emax = hPlanck SpeedOfLight/LMin;
LEDinterp = Interpolation[LED, InterpolationOrder -> 1];

(* Normalized number of photons (per unit time, energy and area)*)
Nph[Ep] :=
LEDinterp[hPlanck SpeedOfLight/Ep]*hPlanck SpeedOfLight/(Ep^3)
Pin = NIntegrate[Ep*Nph[Ep], {Ep, Emin, Emax}];

(* Number of photons above band gap *)
Nsup[Eg] := NIntegrate[Nph[Ep], {Ep, Eg, Emax}];

(* Recombination rate at 0 QFL *)
R0[Eg] :=
2*3.14/(SpeedOfLight*SpeedOfLight*hPlanck^3)*
NIntegrate[Ep^2/(Exp[Ep/(kB*Tcell)] - 1), {Ep, Eg, Emax}]}
APPENDIX A. IDEAL BAD GAP CALCULATION CODE

\[
(* \text{Current Density} *)
\]
\[
\begin{align*}
J(V, Eg) & := e \cdot (Nsup[Eg] - R0[Eg] \cdot \text{Exp}[e \cdot V/(kB \cdot Tcell)]) \\
Jsc[Eg] & := J(0, Eg) \\
Voc[Eg] & := kB \cdot Tcell/e \cdot \text{Log}[Nsup[Eg]/R0[Eg]];
\end{align*}
\]

\[
\begin{align*}
PoutMax[Eg] & := \text{FindMaximum}[(V \cdot J[V, Eg]), \{V, 0\}][[1]] \\
VAtMPP[Eg] & := V/.\text{FindMaximum}[V \cdot J[V, Eg], \{V, 0\}][[2]] \\
JAtMPP[Eg] & := J[VAtMPP[Eg], Eg]; \\
EtaMax[Eg] & := PoutMax[Eg]/Pin; \\
\]

IBGcurve = 
\[
\text{Table}[\{Eg/eV, EtaMax[Eg]\}, \{Eg, 1.1 \text{ eV}, 3 \text{ eV}, 0.05 \text{ eV}\}];
\]
Appendix B

Abeles calculation

Method

Recalling the Fresnel coefficients in both S and P polarization:

- **S polarization**
  \[
  r_k = \frac{\tilde{n}_k q_k - \tilde{n}_{k+1} q_{k+1}}{\tilde{n}_k q_k + \tilde{n}_{k+1} q_{k+1}},
  \]
  \[
  t_k = \frac{2\tilde{n}_k q_k}{\tilde{n}_k q_k + \tilde{n}_{k+1} q_{k+1}}
  \]

- **P polarization**
  \[
  r_k = \frac{\tilde{n}_{k+1} q_k - \tilde{n}_k q_{k+1}}{\tilde{n}_{k+1} q_k + \tilde{n}_k q_{k+1}},
  \]
  \[
  t_k = \frac{2\tilde{n}_{k+1} q_k}{\tilde{n}_{k+1} q_k + \tilde{n}_k q_{k+1}}
  \]
APPENDIX B. ABELES CALCULATION

with \( \tilde{q}_k = \sqrt{1 - \frac{n_0^2 \sin \theta^2}{n_k}} \)

One defines:

- The interface matrix \( I_k \)
  \[
  I_k = \frac{1}{t_k} \begin{pmatrix} 1 & r_k \\ r_k & 1 \end{pmatrix}
  \]
  which relates the electromagnetic waves amplitudes of the interface opposite sides at the coordinate \( z_k \).

- The propagation matrix \( P(z_k, z_{k+1}) \)
  \[
  P(z_k, z_{k+1}) = \begin{pmatrix} e^{j\beta_{k0}} & 0 \\ 0 & e^{-j\beta_{k0}} \end{pmatrix}
  \]
  which changes the amplitude of the electromagnetic waves along the z-axis of the homogeneous layer between \( z_k \) and \( z_{k+1} \) coordinates.

Finally the total matrix is given by:

\[
T_{tot} = I(z_0)P(z_0, z_1)I(z_1)\ldots I(z_{n-1})P(z_{n-1}, z_n)I(z_n) = \begin{pmatrix} T_{11} & T_{12} \\ T_{21} & T_{22} \end{pmatrix}
\]

and \( R \) and \( T \) are simply obtained as follow:

\[
R = \left| \frac{T_{21}}{T_{11}} \right|^2
\]
\[
T = \left| \frac{n_{out}^2}{n_{in}} \frac{1}{T_{11}} \right|^2
\]

The corresponding Mathematica code for reflection and transmission calculations is given.

**Reflection coefficient calculation in S polarization**

```mathematica
ReflectionS[Ni_, No_, lambda0_, theta_, Ns_, Ds_] := Module[
(* ReflectionS derive the reflection coefficient R for S polarization. Arguments: 
Ni: scalar, index of the input medium 
No: scalar, index of the output medium 
lambda0: scalar, vacuum wavelength in nm *)
```


\(\text{theta: scalar, incidence angle of the wavevector in rad}\)

\(\text{Ns: real vector, containing the optical indices of each layer}\)

\(\text{Ds: real vector, containing the layers depth in m}\)

\(\lambda = \lambda_0 \times 10^{-9};\)

\(n = \text{Length}[\text{Ds}];\)

\(f_q[n_] := (1 - (N_i \times \sin[\text{theta}]/n)^2)^{0.5};\)

\(f_b[n_, d_] := 2\pi/\lambda \times d \times n \times f_q[n];\)

\(f_r[n_, n1_] := (n \times f_q[n] - n1 \times f_q[n1])/(n \times f_q[n] + n1 \times f_q[n1]);\)

\(f_t[n_, n1_] := (2 \times n \times f_q[n])/(n \times f_q[n] + n1 \times f_q[n1]);\)

\(P_{kk1} = \text{ConstantArray}[0, \{2, 2\}];\)

\(I_k = \text{ConstantArray}[0, \{2, 2\}];\)

\(M = \text{IdentityMatrix}[2];\)

\((* \text{ Interface matrix 101 from the input region (0) to the first layer (1) } *)\)

\(I_k = 1/f_t[N_i, Ns[[1]]] \times (\text{IdentityMatrix}[2]);\)

\(I_k[[2, 1]] = f_r[N_i, Ns[[1]]] / f_t[N_i, Ns[[1]]];\)

\(I_k[[1, 2]] = I_k[[2, 1]];\)

\(M = I_k;\)

\(\text{If}[n > 1, (* \text{ If there is more than 1 layer } *)\)

\(\text{For}[i = 1, i <= n - 1, i++,

\((* \text{ Definition of the propagation matrix } P(z_k, z_{k+1}) \text{ along the } z-\text{axis in the homogenous layer between } z_k \text{ and } z_{k+1} \text{ coordinates } *)\)

\(P_{kk1}[[1, 1]] = \text{Exp}[I \times f_b[Ns[[i]], Ds[[i]]]];\)

\(P_{kk1}[[2, 2]] = \text{Exp}[-I \times f_b[Ns[[i]], Ds[[i]]]];\)

\((* \text{ Definition of the interface matrix } I(z_k) \text{ which relates the } \text{amplitudes of electromagnetic waves of the opposite sides of the } \text{interface at the coordinate } z_k *)\)

\(I_k = 1/f_t[Ns[[i]], Ns[[i + 1]]] \times (\text{IdentityMatrix}[2]);\)

\(I_k[[2, 1]] = f_r[Ns[[i]], Ns[[i + 1]]] / f_t[Ns[[i]], Ns[[i + 1]]];\)

\(I_k[[1, 2]] = I_k[[2, 1]];\)

\((* \text{ Transfert matrix } M *)\)

\(M = M \cdot P_{kk1} \cdot I_k;\)

\(\text{[\text{]}};\)

\((* \text{ Propagation matrix } P(n-1,n) \text{ in the last layer } *)\)

\(P_{kk1}[[1, 1]] = \text{Exp}[I \times f_b[Ns[[n]], Ds[[n]]]];\)

\(P_{kk1}[[2, 2]] = \text{Exp}[-I \times f_b[Ns[[n]], Ds[[n]]]];\)

\((* \text{ Interface matrix } I(n, \text{out}) \text{ toward the output region } *)\)

\(I_k = 1/f_t[Ns[[n]], No] \times (\text{IdentityMatrix}[2]);\)
APPENDIX B. ABELES CALCULATION

\[ \text{Ik}[[2, 1]] = \frac{f_r[\text{Ns}[[n]], \text{No}]}{f_t[\text{Ns}[[n]], \text{No}]}; \]
\[ \text{Ik}[[1, 2]] = \text{Ik}[[2, 1]]; \]

(* Total transfer matrix M *)
\[ M = M.\text{Pkk1}.\text{Ik}; \]

(* Total reflection coefficient *)
\[ r = \frac{M[[2, 1]]}{M[[1, 1]]}; \]
\[ R = (\text{Abs}[r])^2; \]

Return [R]

Transmission coefficient calculation in S polarization

Calculation is similar to ReflectionS.

TransmissionS[Ni_, No_, lambda0_, theta_, Ns_, Ds_] := Module[
{lambda, n, fq, fb, fr, ft, Pkk1, Ik, M, t, T},
...

(* Total reflection coefficient *)
\[ t = \frac{\text{No}/\text{Ni}}{M[[1, 1]]}; \]
\[ T = (\text{Abs}[t])^2; \]
Return [T]

Reflection coefficient calculation in P polarization

Same calculation as ReflectionS with adapted Fresnel coefficients.

ReflectionP[Ni_, No_, lambda0_, theta_, Ns_, Ds_] := Module[
{lambda, n, fq, fb, fr, ft, Pkk1, Ik, M, r, R},
...

\[ \text{fq}[n_] := (1 - (\text{Ni}*(\text{Sin}[\theta])/n)^2)^{0.5}; \]
\[ \text{fb}[n_, d_] := 2*\text{Pi}/\text{lambda}*d*n*fq[n]; \]
\[ \text{fr}[n_, n1_] := (n1*fq[n] - n*fq[n1])/(n1*fq[n] + n*fq[n1]); \]
\[ \text{ft}[n_, n1_] := (2*n*fq[n])/(n1*fq[n] + n*fq[n1]); \]

...
Return [R]
]
Transmission coefficient calculation in P polarization

Calculation is similar to ReflectionP.

TransmissionS[\(N_l\), \(N_o\), \(\lambda_{0}\), \(\theta_{\pi}\), \(N_s\), \(D_s\)] := Module[
    {\(\lambda\), \(n\), \(fq\), \(fb\), \(fr\), \(ft\), \(Pkk1\), \(Ik\), \(M\), \(t\), \(T\)},

    (* Total reflection coefficient *)
    \(t = No/Ni/M[[1, 1]]\);
    \(T = (Abs[t])^2\);
    Return[T]
]

...
Appendix C

Material indices modelisation

The OptiFDTD software only support dispersive materials fitted with Sellmeier model or Lorentz-Drude model.

Glass (BK7) as well as the Polystyren are fitted with Sellmeier formula:

\[ n_{BK7}^2 - 1 = \frac{1.03961212\lambda^2}{\lambda^2 - 0.00600069867} + \frac{0.231792344\lambda^2}{\lambda^2 - 0.0200179144} + \frac{1.01046945\lambda^2}{\lambda^2 - 103.560653} \]

\[ n_{PS}^2 - 1 = \frac{1.4435\lambda^2}{\lambda^2 - 0.020216} \]

ITO is simulated with Lorentz-Drude model:

\[ \epsilon_r(\omega) = \epsilon_{\infty} + \sum \frac{A_m\Omega_m^2}{\omega_m^2 + j\omega\Gamma_m - \omega^2} \]

With the adaptable parameters:
- \( \epsilon_{\infty} \) the infinite index
- \( N \) the number of resonances
- \( A_m \) the m resonance amplitude
- \( \Omega_m \) the plasma frequency
- \( \omega_m \) the resonant frequency
- \( \Gamma_m \) the damping frequency
Figure C.1: Sellmeier model for Glass and Polystyrene.
## Appendix C. Material Indices Modelisation

### Figure C.2: ITO indices fit.

(13) ITO (In$_2$O$_3$-SnO$_2$, Indium tin oxide), 250nm-850nm

<table>
<thead>
<tr>
<th>m</th>
<th>Strength G</th>
<th>Plasma Frequency</th>
<th>Resonate Frequency</th>
<th>Collision Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.65775021</td>
<td>1.10969183e16</td>
<td>1.10969183e16</td>
<td>6.66988667e12</td>
</tr>
<tr>
<td>2</td>
<td>0.25650701</td>
<td>7.28356123e15</td>
<td>7.28356123e15</td>
<td>2.03518981e15</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>2.41712184e15</td>
<td>0.0</td>
<td>6.92563636e01</td>
</tr>
</tbody>
</table>

Figure C.2: ITO indices fit.