

# Harvesting light energy with optical rectennas

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## ABSTRACT

This work presents investigations about the realisation and modelisation of rectenna solar cells. Rectennas are antennas coupled with a rectifier to convert the alternative current originating from the antenna into direct current that can be harvested and stored. By reducing the size of the antennas to the nano-scale, interactions with visible and near infrared light become possible. If techniques such as nano-imprint lithography make possible the fabrication of sufficiently small plasmonic structures to act as optical antennas, the concept of rectenna still faces several challenges. One of the most critical point is to achieve rectification at optical frequencies. To address this matter, we propose to use molecular diodes that can be self assembled on metallic surfaces. In this paper, we present basic rectenna theory as well as optical simulations of plasmonic structures and first experimental results of samples fabrication.

**Keywords:** Rectenna, Nano-Antennas, Surface Plasmon, Molecular Electronics, Solar Energy

## 1 INTRODUCTION

As predicted by Shockley and Queisser in the 60's, the photoconversion phenomenon involved in mono junctions solar cells has an upper limit of 33% [11]. Other concepts, such as high efficiency tandem solar cells designed to perform under concentrated light have been developed to overcome this limitation [3], but this technology remains expensive and difficult to process to an industrial scale. The concept of optical rectennas goes back to the 70's when Bailey proposed that a nano-scale antenna coupled with a rectifier could harvest electromagnetic waves in the visible and infrared region [2]. Later, Joshi and Moddel built a photon assisted theory and predicted conversion efficiencies close to 100% for a monochromatic rectenna in the visible range. As for the performance under a realistic sun illumination, it was found to be 44% for a single polychromatic rectenna geometry [8]. Unlike the Shockley-Queisser limit, this 44% limit does not rely on the material, but strongly depends on the rectenna geometry. This feature makes rectenna arrays good candidates for tandem-like structures based on several antennas sizes and shapes, result-

ing in a promising low cost process.

Today, nano-imprint lithography (NIL) technologies enable the fabrication of sufficiently small 3D structures to act as optical antennas. As for the rectifier element, metal-insulator-metal (MIM) structures with a very small RC time could be a suitable solution [7], as well as organic molecular electronics which recently shown state of the art rectification ratio  $R = \frac{|I(+1V)|}{|I(-1V)|}$  up to  $10^3$  [12]. Both of these solutions offer the benefit of enabling deposition of very small diodes on the top of each nano-antennas, either by atomic layer deposition (ALD) for the MIM structures [10], or by self assembled monolayer (SAM) for the molecules. A recent work has already demonstrated power production originating from optical rectennas [10], but research in this field remains at stage of proof of concept. In this work, we study and develop rectenna solar cells composed of plasmonic nano-antennas associated with rectifying self-assembled molecular diodes. First we describe the theoretical principle of rectennas and discuss the state of the art concerning analytical modeling. Then we present results of finite difference time domain (FDTD) simulations that are aimed to develop plasmonic structures to enhance local electric field originating from visible and infrared light. Finally we present first results of back electrodes fabrication and deposition of SAMs of rectifying molecules, which are the firsts steps toward a complete rectenna sample.

## 2 BASIC RECTENNA THEORY

An optical rectenna is the combinaison of a nano-antenna and a circuit designed to convert the AC oscillation of electrons into DC current that can be sent to

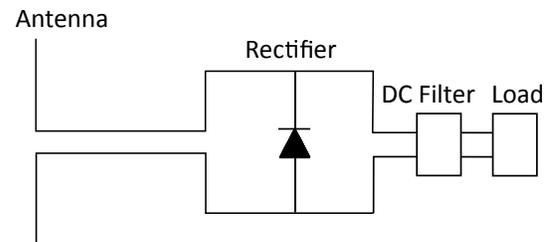


Figure 1: Equivalent electrical circuit of a rectenna

a load as in the case of a standard solar cell. This conversion is carried out by both a diode and a DC filter, as shown Fig.1 in the equivalent electrical circuit.

Rectifying a signal at optical frequencies (up to  $10^3$  THz) requires very fast diodes that cannot be provided by regular semiconductor technology. To overcome this limitation, we propose to use ferrocene alkanethiol molecular diodes which consist in single carbon chains terminated by a ferrocene unit. This molecules have been extensively studied in the past ten years and their robust rectifying ratio [12] make them serious candidates for diverse molecular electronic application. Further informations and results about ferrocene alkanethiols will be discussed in Section 4.

In first approximation, the rectifying phenomenon can be understood by modeling the antenna-molecule-back electrode structure by a MIM tunnel junction [6]. In Fig.2 we represent the three configurations of applied bias. This highlights that a junction constituted by two different work function metals will favor tunnel current under one bias direction (here, positive bias) because of the reduction of the tunneling distance between the left and right electrode. This phenomenon results in a rectification behaviour in the dark. If an external electric field such as visible and infrared light contribute to an additionnal  $V_{ph}$  alternative bias, the tunnel current enhancement would even occur at 0 bias and opposite bias direction (here, negative bias). When the  $I(V)$  characteristic has positive current values for a positive applied bias, the rectenna act as a detector in the first quadrant. When the  $I(V)$  characteristic starts having values of positive current for negative bias, we enter the power production mode in the second quadrant.

Up to now, several attempts to quantitatively model the behaviour of rectenna solar cells have been made. In particular, S.Grover and G.Moddel presented a quantum theory to describe the phenomenon of rectification operating at optical frequencies within an MIM structure [6]. Recently, a model integrating ferrocene alkanethiol molecules sandwiched between two metallic electrodes has been presented [4]. Despite all those efforts, understanding the behaviour of electronic charges within a molecule remains a challenge, as recently outlined by Garrigues [5], who suggested to use experimental datas to find fit parameters that can be applied to the classical Landauer formula to obtain the current density as a function of applied bias, in the particular case of no external illumination.

### 3 PLASMONIC STRUCTURES FOR ELECTRIC FIELD ENHANCEMENT

According to Fig.2, entering the second quadrant under illumination requires a sufficient  $V_{ph}$  alternative bias.

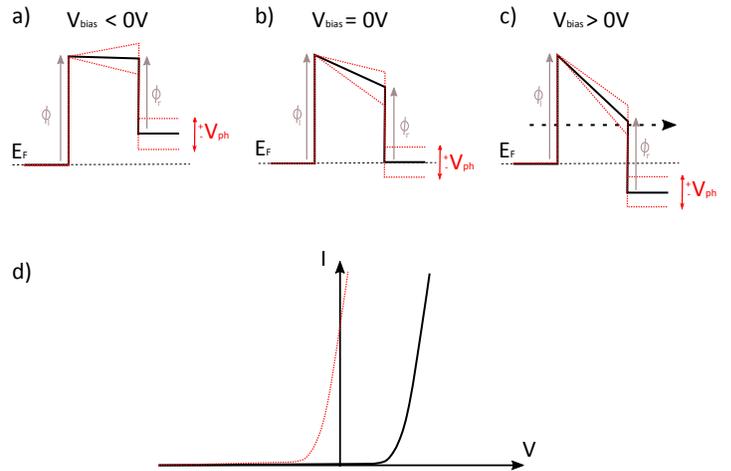


Figure 2: Schematic potential energy level diagram.  $V_{ph}$  denotes the additional bias induced under illumination,  $\phi_l$  and  $\phi_r$  denote the left and right electrode work functions a) at negative bias b) at 0 bias c) at positive bias d) corresponding  $I(V)$  curve for both dark (black solid line) and illumination (dotted red line) situations.

The threshold voltage of the molecular diode is conditioned by the work functions of both electrodes it is connected to. To fix ideas, let us assume that a ferrocenyl alkanethiol molecular diode has a threshold voltage  $V_t = 0.5$  V, which is consistent with values reported in the litterature [13]. In this case, power production from the rectenna device is conditioned by  $V_{ph} \geq 0.5$  V. Considering that the typical size of a molecular rectifier such as ferrocene alkanethiol is about  $d_{mol} = 2$  nm, this results into a required electric field of magnitude  $E = \frac{V_{ph}}{d_{mol}} = 2.5 \cdot 10^8$  V m $^{-1}$ . Yet, even if we consider a polychromatic nano-antenna device able to catch the whole solar spectrum, the expression of Poining vector for an irradiance of  $P_{light} = 1000$  W/m $^2$  yields to an electric field of magnitude  $E_{light} = 8.7 \cdot 10^2$  V m $^{-1}$ , which is still five orders of magnitude below the required value. Thus, two solutions are left to enable rectification in the second quadrant : engineering the work functions of the metal electrodes to reduce the threshold voltage, and enhancing the local electric field collinearly to the molecular diode. This section presents a nano-scale geometry designed to address the latter option.

FDTD simulations were performed using the FDTD module of Lumerical<sup>®</sup> software. Our simulation work was driven by the objective of finding a geometry of nano-antennas that would be easily printable using nano-imprint lithography technology. This would result into a low cost process: printing periodic arrays of nano-antennas into a plastic sheet to obtain a nano-textured substrate that could be easily metalised via e-beam evaporation or sputtering deposition. Fig.3 shows one lattice of such a 3D nano-antennas array that exhibits a local-

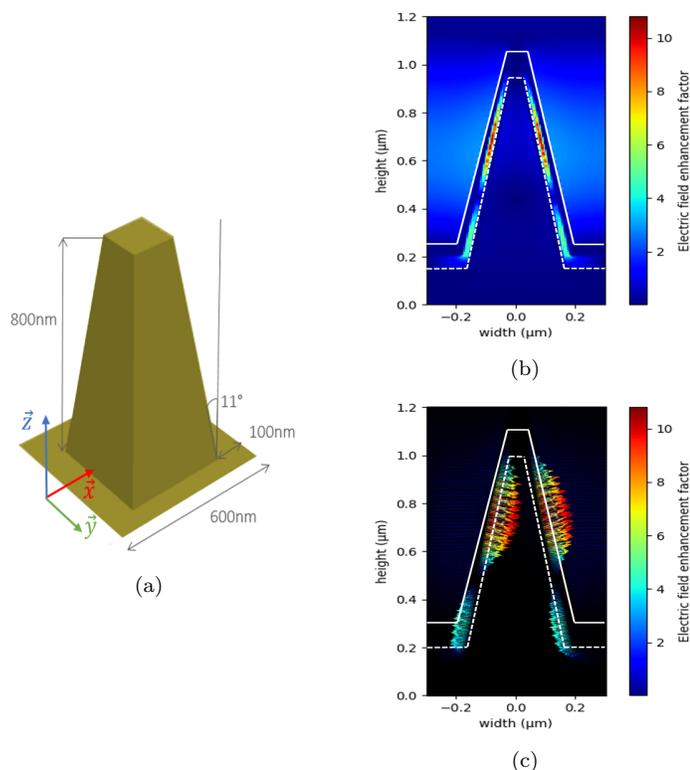


Figure 3: a) 3D rendering of one lattice of the simulated nano-antennas array covered with gold. b)c) results of FDTD simulation in the  $(x, z)$  plane showing b) electric field enhancement factor  $\frac{|E|}{|E_0|}$  for a 1850 nm illumination, c) direction of the enhanced electric. White plain line symbolise the free space / gold interface, white dotted line symbolise the gold / molecules interface

ized electric field enhancement of a factor 10 at 1850 nm. In Fig.3.c) we observe the direction of the localized electric field which corresponds to a surface plasmon oscillation with direction normal to the antenna surface, thus colinear to the molecular diode that would be self assembled upon this metallic surface. As highlined earlier, an enhancement factor of 10 remains too small to expect electrical rectification in the second quadrant unless the work functions of the electrodes are designed to produce a threshold voltage  $V_t < 0.5$  V. Further efforts in this two directions are therefore still needed to achieve power production from a rectenna device.

#### 4 SAMPLE REALISATION

Our fabrication process is divided into the following steps : nano-imprint of the rectenna array into Poly(methyl methacrylate) (PMMA) ; deposition of the bottom electrode ; deposition of a SAM of ferrocene alkanethiols ; deposition of the top electrode. Fig.4 shows the result of gold deposition (30nm) on the nano-imprinted PMMA substrate using e-beam evaporation. We ob-

serve a conformal deposition which preserves the shape of the antenna and the periodicity of the lattice. Then a SAM of 11(Ferrocenyl)undecanethiol, ( $C_{11}H_{32}FeS$ ) purchased from Dojindo Molecular Technologies, was deposited by immersion of the samples into a 3mM ethanolic solution for 24 hours. In order to get a direct proof of the adsorption of the molecules on the nano-textured gold substrate, we performed cyclic voltammetry measurements with an aqueous 1.0 M  $HClO_4$  solution as electrolyte. The voltammograms are shown Fig.5 for several voltage sweep rates and display typical potential peaks for oxydation and reduction of the iron unit, thus proving the presence of the molecules on the nano-antenna array.

Next step will consist in electrical measurements at a microscopic scale to detect rectification both under dark and illumination conditions. Finally, the deposition of a top electrode should permit the collection of charges and macroscopic scale electrical measurements. This last step has been reported as being challenging due to the fragility of the SAMs, and is known to introduce electrical shorts [9][1]. As a consequence it requires the fabrication of a significant number of samples to get statistical results that can lead to conclusions.

#### 5 CONCLUSION AND FURTHER WORK

In this work, we presented a theoretical analysis of basic principles that rule the operation in an optical rectenna device. In particular, to achieve power production at visible and infrared frequencies, we highlighted the necessity to act both on the difference of work function of bottom and top electrode and on the electric field enhancement within the nano-antennas array. To address the latter point, we worked on FDTD simulation of printable solutions of nano-antennas array that exhibit surface plasmon resonance within the visible and

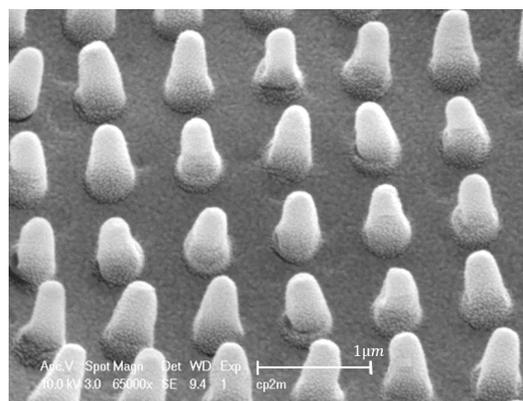


Figure 4: Electron microscope image of a PMMA nano-textured substrate covered with 30 nm of gold

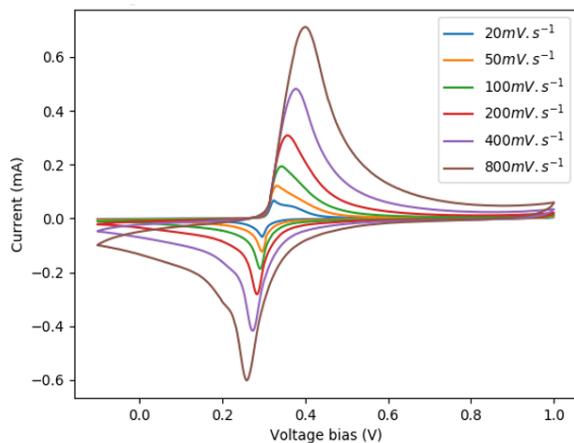


Figure 5: Voltammogram of 11-ferrocene-1-undecanethiols self assembled on a nano-textured gold substrate

infrared range. Amplification ratio of magnitude 10 was found at 1850 nm for a pyramidal structure, with electric field components directed normal to the pyramid surface, thus collinear to the molecular diode orientation. Finally, results of the two first steps of the experimental process have been presented : successful deposition of gold on PMMA nano-structured substrate and self assembly of ferrocene alkanethiol molecular diodes.

Further work will consist in the optimization of the nano-antennas' shape to achieve greater electric field enhancement and both microscopic and macroscopic electrical measurement to detect rectification in dark and illumination conditions.

## REFERENCES

[1] Hylke B. Akkerman, Auke J. Kronemeijer, Jan Harkema, Paul A. van Hal, E. C P Smits, Dago M. de Leeuw, and P. W M Blom. Stability of large-area molecular junctions. *Organic Electronics: physics, materials, applications*, 11(1):146–149, 2010.

[2] R. L. Bailey. A Proposed New Concept for a Solar-Energy Converter. *Journal of Engineering for Power*, 94(2):73, 1972.

[3] Frank Dimroth, Matthias Grave, Paul Beutel, Ulrich Fiedeler, Christian Karcher, Thomas N. D. Tibbits, Eduard Oliva, Gerald Siefert, Michael Schachtner, Alexander Wekkeli, Andreas W. Bett, Rainer Krause, Matteo Piccin, Nicolas Blanc, Charlotte Drazek, Eric Guiot, Bruno Ghyselen, Thierry Salvétat, Aurélie Tauzin, Thomas Signamarcheix, Anja Dobrich, Thomas Hannappel, and Klaus Schwarzborg. Waferbonded four-junction GaInP/GaAs//GaInAsP/GaInAs concentrator solar cells with 44.7% efficiency. *Prog. Photovolt: Res. Appl.*, 22(January 2014):277–282, 2014.

[4] David Duche, Ujwol Planchoke, Florian-xuan Dang, Judikael Le Rouzo, Marc Bescond, Jean-jacques Simon, Teodor Silviu Balaban, Ludovic Escoubas, David Duche, Ujwol Planchoke, Florian-xuan Dang, and Judikael Le Rouzo. Model of self assembled monolayer based molecular diodes made of ferrocenyl-alkanethiols. *Journal of Applied Physics*, 115503, 2017.

[5] Alvar R. Garrigues, Li Yuan, Lejia Wang, Eduardo R. Mucciolo, Damien Thomson, Enrique del Barco, and Christian a. Nijhuis. A Single-Level Tunnel Model to Account for Electrical Transport through Single Molecule- and Self-Assembled Monolayer-based Junctions. *Scientific Reports*, 6(February):26517, 2016.

[6] Sachit Grover, Saamil Joshi, and Garret Moddel. Quantum theory of operation for rectenna solar cells. *J. Phys. D: Appl. Phys. J. Phys. D: Appl. Phys.*, 46(46):135106–7, 2013.

[7] Sachit Grover and Garret Moddel. Applicability of Metal/Insulator/Metal (MIM) diodes to solar rectennas. *IEEE Journal of Photovoltaics*, 1(1):78–83, 2011.

[8] Saamil Joshi and Garret Moddel. Efficiency limits of rectenna solar cells: Theory of broadband photon-assisted tunneling. *Applied Physics Letters*, 102(8):1–5, 2013.

[9] Christian A. Nijhuis, William F. Reus, Jabulani R. Barber, Michael D. Dickey, and George M. Whitesides. Charge transport and rectification in arrays of SAM-based tunneling junctions. *Nano Letters*, 10(9):3611–3619, 2010.

[10] Asha Sharma, Virendra Singh, Thomas L Bougher, and Baratunde A Cola. A carbon nanotube optical rectenna. *Nature nanotechnology*, 10(12):1027–1032, 2015.

[11] William Shockley and Hans J. Queisser. Detailed balance limit of efficiency of p-n junction solar cells. *Journal of Applied Physics*, 32(3):510–519, 1961.

[12] Li Yuan, Rochus Breuer, Li Jiang, Michael Schmitt, and Christian A. Nijhuis. A Molecular Diode with a Statistically Robust Rectification Ratio of Three Orders of Magnitude. *Nano Letters*, 15(8):5506–5512, 2015.

[13] Li Yuan, Nisachol Nerngchamngong, Liang Cao, Hicham Hamoudi, Enrique del Barco, Max Roemer, Ravi K Sriramula, Damien Thomson, and Christian a Nijhuis. Controlling the direction of rectification in a molecular diode. *Nature communications*, 6:6324, 2015.