3.2. DESCRIPTION DES TRAVAUX PAR TACHE / DESCRIPTION BY TASK

TASK 1: COORDINATION OF THE PROJET (CIMAP)

The work coordination will include:

1. *The administrative and financial management of the project:* the coordinator will be the ANR contact and will manage the various reports to be submitted periodically. He will also write the consortium agreement which is signed by all partners before the end of the first year of the project.
2. *The scientific management of the project*: the coordinator is responsible for the writing of the minutes of the biannual meetings as well as the scientific reports. He is responsible for managing deliverables and milestones of the project and must ensure the coordination between all the tasks. Each task has one of the project partners as a scientist leader.
3. *Communication*: the coordinator will be responsible for disseminating information within the consortium, but also towards institutions and local actors with the help of the communication cell in order to promote and to communicate the work done in this project. In addition, the coordinator is responsible for writing the annual progress reports in relation with those responsible for each task. These reports are validated by the consortium before being sent to the ANR. From the viewpoint of publications and conferences, a summary is sent in advance for the consortium agreement. The coordinator will work closely with the team responsible of the communication to promote the results that will be achieved throughout the project.
4. *Promotion*: the promotion strategy is detailed in item 4.

TASK 2: NANOSTRUCTURED SUBSTRATE (D. STIEVENARD, IEMN)

TASK 2	
Title	**Nanostructured Substrate**
Duration	42 months
Scientific Leader	D. Stievenard (IEMN)
Partners	CIMAP
Goal	Fabrication of an optimized nanostructured substrate
Deliverables-Milestones	• **L2.1:** Intermediate report on the nanostructured material, nanocones • **J2.1 :** Shape optimization depending on the simulation, SEM imaging • **L2.2:** Final report on the nanostructured material, nanocones • **L2.3 :** Intermediate report on the nanocones with p-n junction • **J2.2 :** Final report on the nanocones with p-n junction
Success Indicator	• Fabrication of a nanostructured substrate (nanocones) with good optical properties • p-n junction on nanocones.

1. ***Subtask 2.1 : Nanocones (IEMN)***

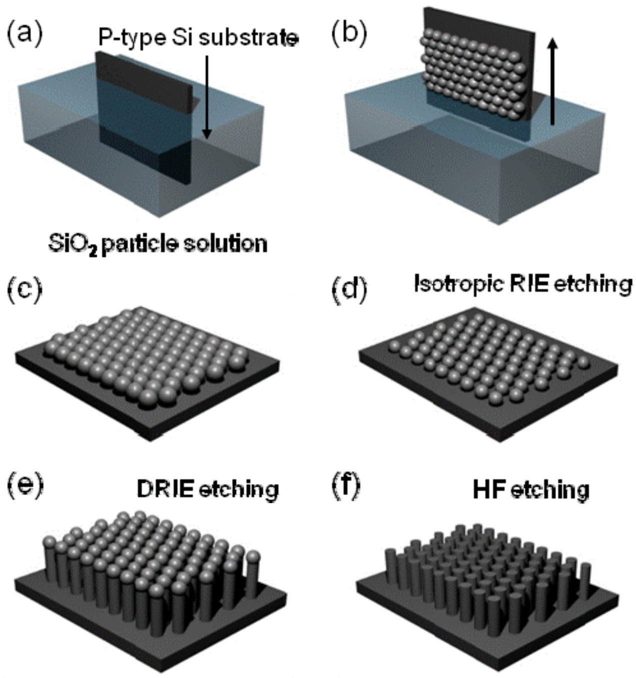


Figure 5: Etching process

Basically, the absorption obviously plays a major role on the yield of a solar cell. Recent publications show that the Lambertian limit can be achieved by using either a nanostructuration of the surface or nanowires (NWs) often obtained by CVD or by an etching process to allow the fabrication of nanocones. IEMN has developed such an approach within a DGA contract (DGA contract REI 34 2008 0031). For the etching, the use of electron beam lithography is avoided using silica balls as a mask for etching[56-57]. These balls are deposited by Langmuir Blodgett technique. The diameter determines the distance between the nanocones. Before fabricating them, the ball size can be reduced by a soft etching to adjust the final diameter. During the etching, the diameter of the ball decreases, which leads naturally to a conical shape. The process is described in Figure 5 in the case of NW. Figure 6 is an SEM image of Si nanocones obtained by this method.

In order to minimize the reflectance of the structure, a study of the reflectance versus the size (height, diameter, shape) will be done. The best shape will be taken for the solar cell structures.

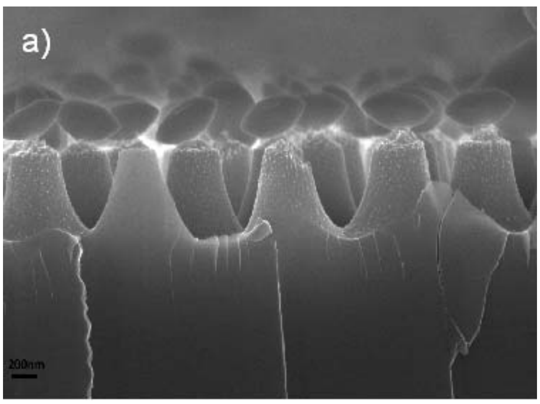
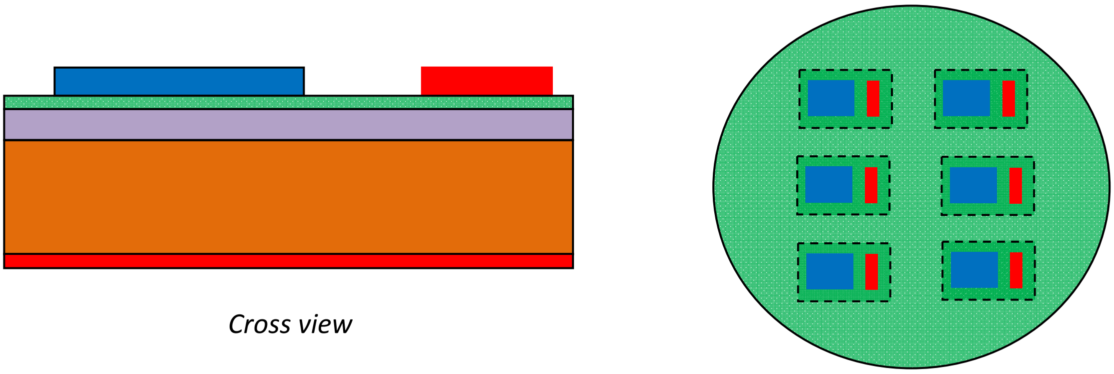


Figure 6: SEM image of nanocones obtained by etching process

2. *Subtask 2.2 : Nanocones ; p-n Junction (IEMN)*

The separation of excitons requires an electric field created by a p-i-n junction in our case. Starting from p-type (doping of about 10^{18} Bore/cm^3) substrate, a typically 250 nm intrinsic polysilicon layer, followed by a 50-80 nm nanometers polysilicon doped n^+ layer will be deposited by LP-CVD technique available at IEMN.
Therefore, the DC layer will be deposited through a mask (realized at IEMN) and it will cover a part of the surface. To collect the carriers, a metal contact in front zone will be made by evaporating aluminum or gold through an other mask and a rear ohmic contact will be made onto the substrate. Cross and top views of the structure are shown in figure 7.



Cross view

Top view

Figure 7 : Schematic cross and top views of the p-n junction fabricated. Correspondence layer- color : In red, metallization, in blue, Down converter layer, in violet, Intrinsic layer, in green, N^+ layer and in orange, P-doped substrate.

As the DC layer needs a thermal annealing (typically 20 min to 1 hour, at temperature ranging from 500 to 750°C), a diffusion of the dopants (Boron and Phosporous) is possible towards the intrinsic layer. In such a case, the n+-i-n junction will be destroyed.
In fact, taking an upper value of the diffusion coefficient of the dopants (see "Intrinsic Point Defects, Impurities and their Diffusion in Silicon", P. Pichler, Springer Verlag, Wien, 2004), namely 6 x 10^{-16} cm^2 /s (corresponding to Boron diffusion coefficient and three times the Phosphorous one), a maximum temperature of 750°C for 1 hour, we calculate a diffusion length of 14 nm for Boron and 10 nm for Phosphorous. Therefore, we estimate an intrinsic layer with a minimum thickness of 250-30-20 = 200 nm, a typical value for thin layer solar cells. The annealing temperature of the DC layer will be optimized to avoid problems with the diffusion of dopants.
To compare the efficiency of nanostructured structures, two approaches will be done in parallel, i.e. a classical planar structure or nanostructured one, with and without the DC layer.

The risk of this task concern the annealing treatment applied for the DC layer. This later will be optimized in the following tasks (tasks 3 and 4) with respect to the constraints of the *dopant diffusion. As shown in figure 3, concerning the Tb^{3+}, an intense emission is already achieved in a SiN_x layer after annealing at 600°C.*

TASK 3 : ASSI :RE(PR,TB)$^{3+}$:YB^{3+} SYSTEM (F. GOURBILLEAU, CIMAP)

TASK 3	
Title	AsSi :RE(Pr,Tb)$^{3+}$:Yb^{3+} System
Duration	48 months
Scientific Leader	F. Gourbilleau (CIMAP)
Partners	
Goal	Fabrication of an optimized $Si_xO_yN_z$:RE^{3+}(Pr^{3+},Tb^{3+})/SiO_2:Yb^{3+} multilayers.
Deliverables-Milestones	• **L3.1:** Intermediate report on the growth of thin films doped with Atomic Scale Si sensitizers and Pr^{3+}-Yb^{3+} ions. • **J3.1:** Final report on the $Si_xO_yN_z$:Pr^{3+}/SiO_2:Yb^{3+} multilayers fabrication • **L3.2:** Intermediate report on the growth of thin films doped with AsSi and Tb^{3+}-Yb^{3+} ions. • **J3.2:** Final report on the $Si_xO_yN_z$:Tb^{3+}/SiO_2:Yb^{3+} multilayers fabrication
Success Indicator	• Achievement of an intense Pr^{3+} emission • Achievement of an intense Tb^{3+} emission • Achievement of a high quantum yield in the $Si_xO_yN_z$:Pr^{3+}/SiO_2:Yb^{3+} system. • Achievement of a high quantum yield in the $Si_xO_yN_z$:Tb^{3+}/SiO_2:Yb^{3+} system

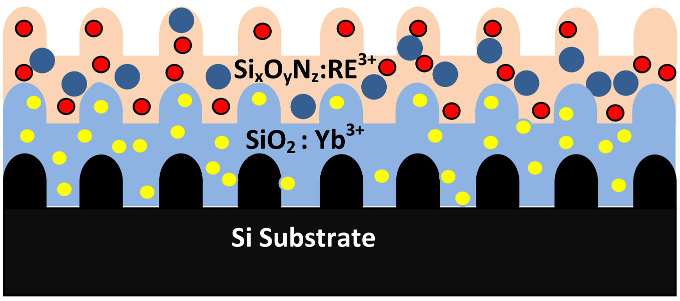


Figure 8 : Drawing of the Multilayer fabricated. RE = Pr^{3+} or Tb^{3+}. ○ :Yb^{3+} ;● :Pr^{3+} or Tb^{3+} ; ● : Atomic Scale Si.

The objective of this task is to produce ML structures consisting in stacking of RE-doped Si-rich-SiON sublayers ($Si_xO_yN_z$) and Yb^{3+}-doped silica sublayers on a nanostructured substrate (Fig. 8). The Atomic scale Si sensitizers density and size, Yb^{3+} and RE^{3+} (Tb^{3+} or Pr^{3+}) ion concentration are the key parameters that will determine the efficiency of the energy transfer AsSi:RE^{3+}:Yb^{3+}. The films produced during this project will be analyzed in Task 5 to optimize the coupling Atomic Scale Si sensitizers:RE^{3+}(Tb^{3+} or Pr^{3+}): Yb^{3+} and thus achieve the goal of an efficient DC layer.

1. *Subtask 3.1 : $Si_xO_yN_z$:Pr^{3+}/SiO_2:Yb^{3+} Multilayers (CIMAP)*

The growth of the films will be performed on Si substrates by a reactive or classical co-sputtering process, to study and optimize the Pr-doped system. The deposition parameters (plasma pressure, temperature, RF power, etc. ..) will allow to achieve an engineering of the microstructure and doping at the nanometer scale as shown by various studies of RE-doped systems(7-8,11). The co-sputtering approach using separate target allows to control accurately the incorporation of the different species in the layer by monitoring separately the RF power applied on each cathode.
ML structure will allow both to manage the size of the sensitizers, the location of the two ions and thus the key parameter which is the distance sensitizers:Pr^{3+} and Pr^{3+}:Yb^{3+}. This will be an additional advantage in the control of non-radiative processes involved in such systems such as migration or cross relaxation that would be harmful to the final quantum yield. A study of post-deposition annealing via classical annealing or flash annealing will be performed to obtain an optimal quantum yield.

2. *Subtask 3.2 : $Si_xO_yN_z$:Tb^{3+}/SiO_2:Yb^{3+} Multilayers (CIMAP)*

For this system, the same procedure described in Subtask 3.1 will be addressed with the use of either a Tb_4O_7 or Tb targets. Particular attention will be paid to the Tb^{3+}:Yb^{3+} interaction distance as it governs the transfer efficiency in a cooperative process. The multilayer approach which allows controlling the doping of each layer but also the distances between each layer will be a key asset.

The risks of this task are mainly the optimization of the coupling between the Atomic scale Si sensitizer:RE^{3+}(Pr^{3+} or Tb^{3+}) and RE^{3+}:Yb^{3+}. The ML approach is an asset to achieve the objective of demonstrating the existence of such a coupling. Thus, it allows to control the distance between each sublayer, i.e. each rare earth ion and sensitizers, by monitoring the thickness of these sublayers. The problem of energy back transfer that can occur mainly in the AsSi:Pr:Yb system could be overcome by the use of an appropriate matrix such as the HfSiO for which an efficient excitation of Pr^{3+} ions has been already achieved (See Fig.3). The crystalline (monoclinic or tetragonal) or amorphous nature of this matrix can be controlled through the annealing treatment applied(16,58). The experience of CIMAP in the field of engineering nanoscaled layers of different natures will allow to overcome these critical steps, by making optimal nanostructures due to a fine control of (i) the sublayer thicknesses during the growth and (ii) the concentration of the different rare earth ions through the RF power applied on the different targets involved in the fabrication process.

TASK 4 : AG-NP:RE(PR,TB)$^{3+}$:YB^{3+}, AG-NP:ASSI:RE(PR,TB)$^{3+}$:YB^{3+} SYSTEMS (M. CARRADA, CEMES)

TASK 4	
Title	Ag-Np:RE(Pr,Tb)$^{3+}$:Yb^{3+}, Ag-Np:AsSi:RE(Pr,Tb)$^{3+}$:Yb^{3+} Systems
Duration	36 months
Scientific Leader	C. Carrada (CEMES)
Partners	CIMAP
Goal	Fabrication of an optimized Ag-Np :$Si_xO_yN_z$:RE(Pr,Tb)$^{3+}$/SiO_2:Yb^{3+} multilayers.
Deliverables-Milestones	• **L4.1 :** Intermediate report on the growth of $Si_xO_yN_z$:Ag/$Si_xO_yN_z$:Pr^{3+}/SiO_2:Yb^{3+} multilayers • **J4.1 :** Final report on the growth of $Si_xO_yN_z$:Ag/$Si_xO_yN_z$:Pr^{3+}/SiO_2:Yb^{3+} multilayers • **L4.2:** Intermediate report on the growth of $Si_xO_yN_z$:Ag/$Si_xO_yN_z$:Tb^{3+}/SiO_2:Yb^{3+} multilayers • **J4.2 :** Final report on the growth of $Si_xO_yN_z$:Ag/$Si_xO_yN_z$:Tb^{3+}/SiO_2:Yb^{3+} multilayers
Success Indicator	• Enhancement of the Pr^{3+} emission with the presence of Ag-Nps • Enhancement of the Tb^{3+} emission with the presence of Ag-Nps • Achievement of a high quantum yield in the $Si_xO_yN_z$:Ag/$Si_xO_yN_z$:Pr^{3+}/SiO_2:Yb^{3+} system. • Achievement of a high quantum yield in the $Si_xO_yN_z$:Ag/$Si_xO_yN_z$:Tb^{3+}/SiO_2:Yb^{3+} system

The objective of this task is to use multilayer structures optimized in Task 3 to introduce Ag-Nps by ion implantation at low energy. The MLs produced will consist of a stack of (i) an Yb^{3+}-doped SiO_2 and a RE-doped $Si_xO_yN_z$ sublayers (Fig. 9)[1]. An oxide or nitride layer will be deposited above to implant Ag ions. The choice of the nature of the layer to be implanted is related to the need of a plasmon frequency energetically as high as possible (400-430 nm) in order to benefit from the energy transfer of Ag-Np:AsSi and/or Ag-Np:RE^{3+} at high energy. The nature of the layer $Si_xO_yN_z$ (SiN, SiON or SiO_2) will be determined in Task 5 depending on the result of emission properties of the RE ions achieved and in task 6 concerning the suitable matrix for the plasmon frequency expected. An important point will be to monitor and study the effect of the Ag-Nps and their size on the optical properties measured in task 5.

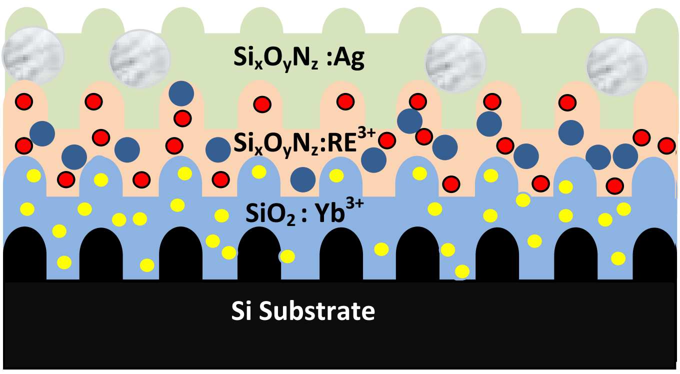


Figure 9 : Schematic drawing of the multilayer structure fabricated with the Ag-Np. RE = Pr^{3+} or Tb^{3+}. :Yb^{3+} ; :Pr^{3+} or Tb^{3+} ; : Atomic Scale Si.

1. *Subtask 4.1 : $Si_xO_yN_z$:Ag / $Si_xN_yO_z$:Pr^{3+} / SiO_2:Yb^{3+} Multilayers (CEMES, CIMAP)*

The Pr^{3+}:Yb^{3+}-doped MLs optimized in Subtask 3.1 will be used here. This structure will be covered with a $Si_xO_yN_z$ layer having a refractive index and a thickness defined in Task 6. The Ag-Np will be formed after implantation at CEMES by means of low-energy implantation well controlled since ten years in this lab. The thicknesses of $Si_xO_yN_z$:Pr^{3+} and SiO_2:Yb^{3+} sublayers will be defined taking into account the process of interaction between the RE ions..

2. *Subtask 4.2 : $Si_xO_yN_z$:Ag/ $Si_xN_yO_z$:Tb^{3+} / SiO_2:Yb^{3+} Multilayers (CEMES, CIMAP)*

For this system, the same procedure described in Subtask 4.1 will be addressed with the use of Tb_4O_7 or Tb targets as described in Subtask 3.2

The risks of this work are those previously described in Task 3 and concern (i) the coupling Ag-Np:RE^{3+}, Ag-Np:AsSi:RE^{3+} and RE^{3+}:Yb^{3+} (ii) the control of the implantation conditions to achieve the optimal Ag-Np size, (iii) the distances Ag-Np:RE^{3+}, Ag-NP:AsSi:RE^{3+} and RE^{3+}:Yb^{3+}. Again, the multilayer approach is a major asset to achieve this best coupling. To obtain high absorption of light, the size and density of Ag-Np in the $Si_xO_yN_z$ layer will be optimized to achieve the required optical properties. Ionic mixing of the interfaces due to implantation technique will be to master. However, CEMES lab has already demonstrated its skill in this field by growing 2D networks of Si nanoparticles and more recently of Ag nanoparticles at a controlled distance from the substrate (see refs. 54 and 59). Moreover, recent results have shown that double layers of Si and Ag nanoparticles at nanometric distances can be obtained by low energy ion implantation thanks to an accurate choice of the fabrication parameters. It must be notice that the use of low to ultra-low energy ion implantation allows to avoid the creation of implantation related defects. CEMES lab has evidenced the possibility to achieve good optical properties in Si-implanted SiO_2 thin films after an appropriate thermal annealing treatment(60). The resonant transfer Ag-Np:RE^{3+} will be demonstrated. A solution to facilitate this transfer will be to implant the Ag ions in the Pr^{3+}- or Tb^{3+}-sublayer. To analyse the effect of Ag-Np localization on the optical properties, configuration using a transparent substrate will be used(61).

TASK 5: MICROSTRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES (M. CARRADA CEMES AND D. STIEVENARD IEMN).

TASK 5	
Title	Microstructural, optical and electrical properties
Duration	48 months
Scientific Leader	M. Carrada (CEMES) – D. Stievenard (IEMN)
Partners	CIMAP
Goal	Microstructural, optical and electrical characterization of the produced layers
Deliverables-Milestones	• **L5.1 :** Report on the optical characteristics of $Si_xO_yN_z:Pr^{3+}/SiO_2:Yb^{3+}$ multilayers • **L5.2 :** Report on the optical characteristics of $Si_xO_yN_z:RE^{3+}$(Pr, Tb)/$SiO_2:Yb^{3+}$ and $Si_xO_yN_z:Ag/SiO_2:Pr^{3+}/SiO_2:Yb^{3+}$ multilayers • **J5.1 :** Quantum yield of $Si_xO_yN_z:Pr^{3+}/SiO_2:Yb^{3+}$ multilayers • **L5.3 :** Report on the optical characteristics of $Si_xO_yN_z:Ag/Si_xO_yN_z:RE(Pr,Tb)^{3+}/SiO_2:Yb^{3+}$ multilayers • **L5.4 :** Report on the optical characteristics of $Si_xO_yN_z:Ag/Si_xO_yN_z:RE(Pr,Tb)^{3+}/SiO_2:Yb^{3+}$ multilayers • **L5.5 :** Report on the photocurrent measurements of $Si_xO_yN_z:Ag/Si_xO_yN_z:RE(Pr,Tb)^{3+}/SiO_2:Yb^{3+}$ multilayers • **J5.2 :** Quantum yield of $Si_xO_yN_z:Tb^{3+}/SiO_2:Yb^{3+}$ multilayers • **L5.6 :** Report on the photocurrent measurements on $Si_xO_yN_z:Ag/Si_xO_yN_z:RE(Pr,Tb)^{3+}/SiO_2:Yb^{3+}$ multilayers • **J5.3 :** Quantum yield of $Si_xO_yN_z:Ag/Si_xO_yN_z:RE(Pr,Tb)^{3+}/SiO_2:Yb^{3+}$ multilayers
Success Indicator	• Achievement of a high quantum yield in the $Si_xO_yN_z:Ag/Si_xO_yN_z:Pr^{3+}/SiO_2:Yb^{3+}$ system. • Achievement of a high quantum yield in the $Si_xO_yN_z:Ag/Si_xO_yN_z:Tb^{3+}/SiO_2:Yb^{3+}$ system. • Evidence of a photocurrent enhancement in $Si_xO_yN_z:Ag/Si_xO_yN_z$:RE (Pr,Tb^{3+})/$SiO_2:Yb^{3+}$ system.

The objective of this work is to study the microstructural, optical and electrical characteristics of the different system fabricated in tasks 2, 3 and 4.

1. *Subtask 5.1 : Microstructure (CEMES, CIMAP, IEMN)*

The layers produced will be analyzed using techniques available in laboratories. These include infrared absorption techniques (FTIR, ATR-FTIR), Raman, X-ray diffraction and AFM available at CIMAP, SEM at IEMN. The ability to perform fine analyzes of the ML microstructure using the technique of Energy Filtered Transmission Electron Microscopy (EFTEM) and Electron Energy Loss Spectroscopy (EELS), available at CEMES is an asset because it will determine the atomic scale sensitizers density (if visible) and the RE ions distribution. The SIMS technique will also be used to determine the dopant concentrations.

Concerning the implanted structures, a new powerful tool for non-invasive physical properties of nanosystems developed by CEMES will be used. It gives the possibility to make at the same point spectroscopic analysis under laser light (4 lines available in the visible) or under illumination with white light (bright field or dark field). Recent results in the CEMES team[(62)] have already demonstrated the suitability of using this technique in the Ag-NP-SiO_2/Si system.

2. *Subtask 5.2 : Optical properties (CEMES, CIMAP)*

This part concerns the study of AsSi:RE(Pr^{3+}or Tb^{3+}), Ag-Np:AsSi, Ag-Np:RE(Pr^{3+}or Tb^{3+}) and RE(Pr^{3+}or Tb^{3+}):Yb^{3+} coupling. The optical characteristics are studied by ellipsometry, PL and PLE spectroscopies and spectrophotometry at CIMAP and CEMES. The quantum yields of the systems will be determined in order to choose, after 36 months (J5.1-J5.2), the optimal system. A dynamic study will be conducted to analyze the speed of transfer and the mechanism involved between different couples analyzed. The values of the lifetime and emission cross sections will be determined for giving data required by the simulations. In this subtask, a fine spectroscopic study will be conducted to analyze the effect of the presence of Ag-Nps on (i) the increase of the absorption of the system (ii) the increase of the luminescence ion Pr^{3+} and Tb^{3+}, and therefore as part of an optimal coupling of the Yb^{3+} ion. Again, as in the previous subtask, determination of lifetime and quantum yield will be carried out.

3. *Subtask 5.3 : Electrical properties (IEMN)*

One of the ways to control the photoelectric efficiency of a system is the measurement of the photocurrent. This latter is the direct image of the carriers generated through the optical absorption and different mechanisms of energy transfer between Atomic scale Si sensitizers, -Ag, and RE ions and the nanocones. For this, IEMN have a measuring bench built around a monochromator, a synchronous detection, all controlled by a PC. The energy spectroscopic scan typically ranges between 1.1 eV to 3.5 eV, perfectly adapted to the energy range of the systems studied. The measurements require the fabrication of p-n junctions (see subtask 2.2) and electrodes.

On the different final optimized structures, current – voltage measurements will be carried out by using a solar cell tester (NPC NCT- 180AA-T) under AM1.5G illumination in order to determine the efficiency of the structure.