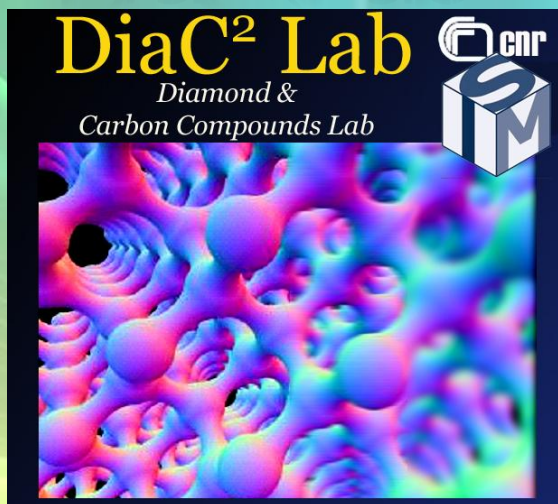


DiaC² Lab

Diamond and Carbon Compounds Laboratory



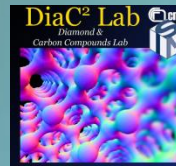
Innovative Solid-State Conversion Technologies for Solar Concentrating Systems

Daniele M. Trucchi

Institute for Structure of Matter (ISM)
of the Italian National Research Council (CNR)
Montelibretti Section

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High-Temperature Thermionic Thermoelectric Concentrated Solar Generators

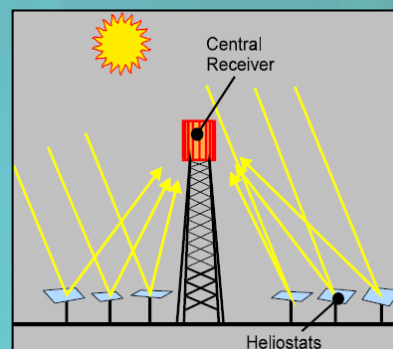
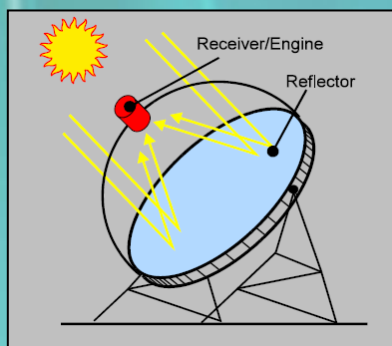
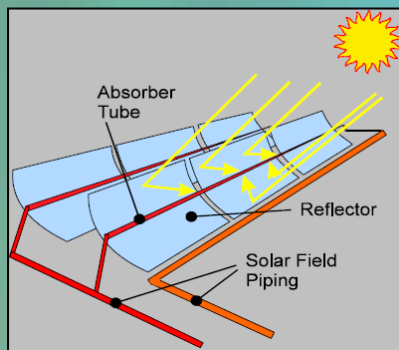
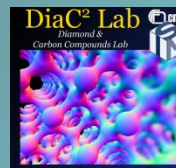
High-Temperature Solar Cells for Concentrated Sunlight

Integration of Complementary Technologies

Other Applications

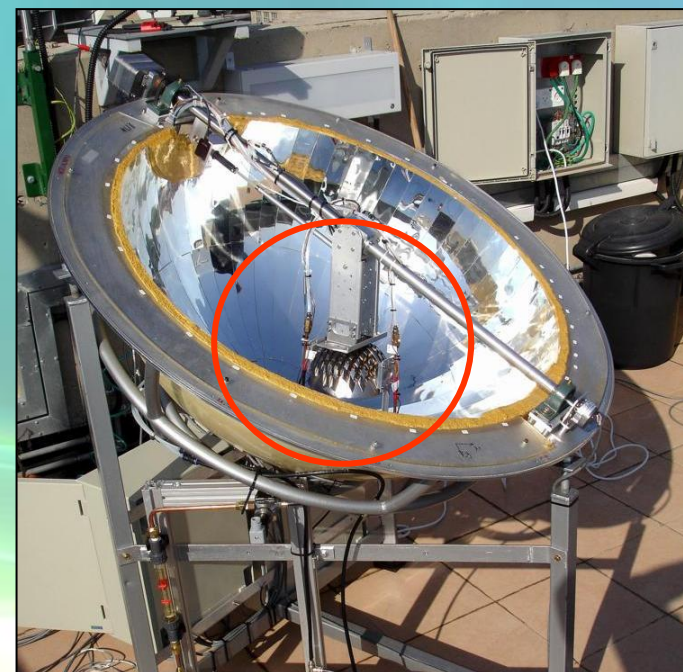


Energy Conversion from Solar Concentrating Systems

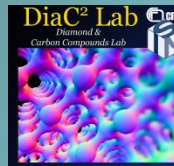


- Linear parabolic collectors (2D system)
- Parabolic dishes (3D system)
- Solar Tower (3D system)

- Less expensive than distributed photovoltaics per unit surface
- Possibility to reach high temperatures (chemical reactions)
- Possibility to co-generate (generation of electric power + **thermal power**)

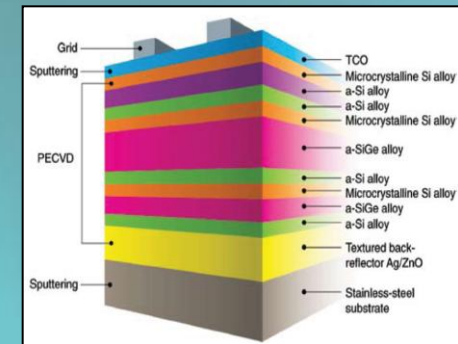


Technologies for Solar Concentrating Systems



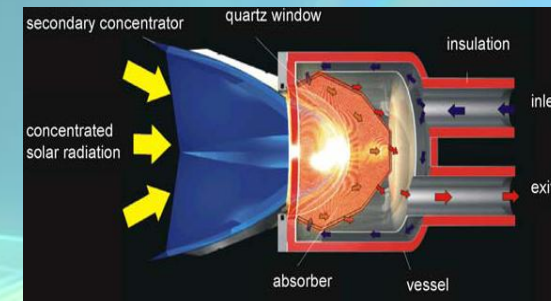
• Concentrated Photovoltaics (CPV)

- ✓ Multiple junction solar cells have a conversion efficiency >45%
- ✓ Compactness
- ✓ No mechanical parts in movement (solid-state)
- Highly Expensive (MBE Fabrication)
- Mandatory need of cooling (conversion efficiency decreases with temperature)
- Degradation with hot-spots
- Production dependent on semiconductor industry (few large-scale world suppliers)

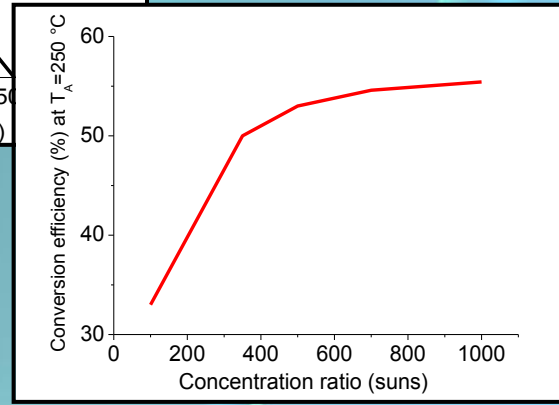
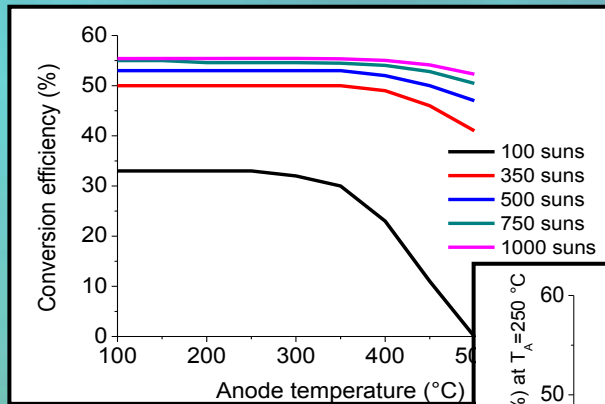
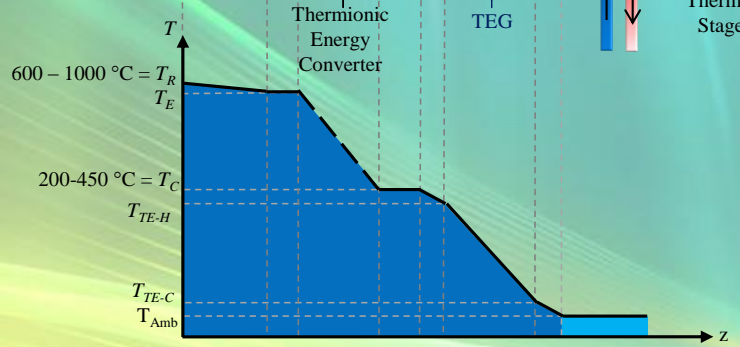
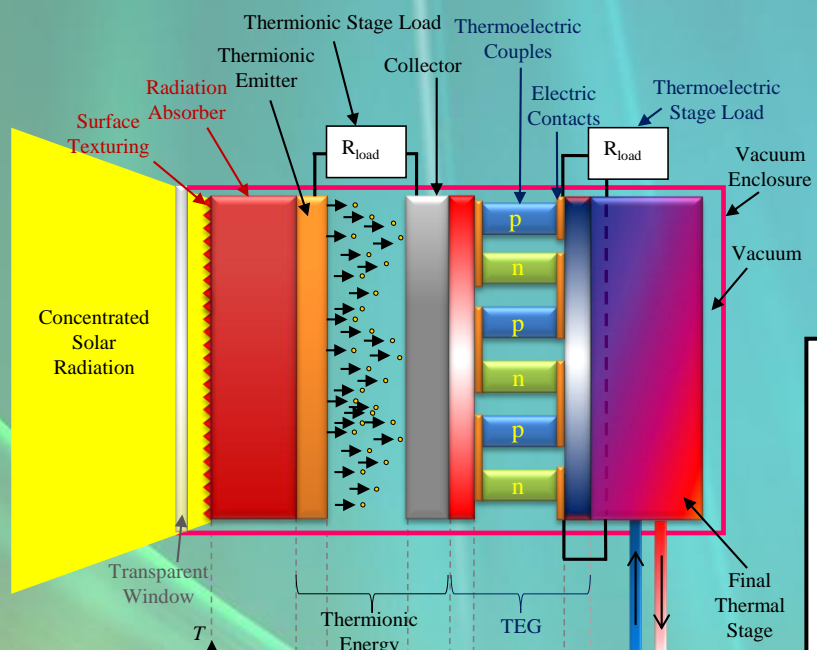


• Thermodynamic Conversion by Heat Engines (Stirling, Rankine) - CSP

- ✓ High temperature operations (<700 °C)
- ✓ Nominal thermal-to-electric conversion efficiency of 35% at high temperatures (> 600 °C)
- Not Compact System
- Mechanical parts in movement -> degradation with operative time
- Economically reasonable for large plants (> 20 kWe)



3rd Alternative: Solar Thermionic-Thermoelectric Generators



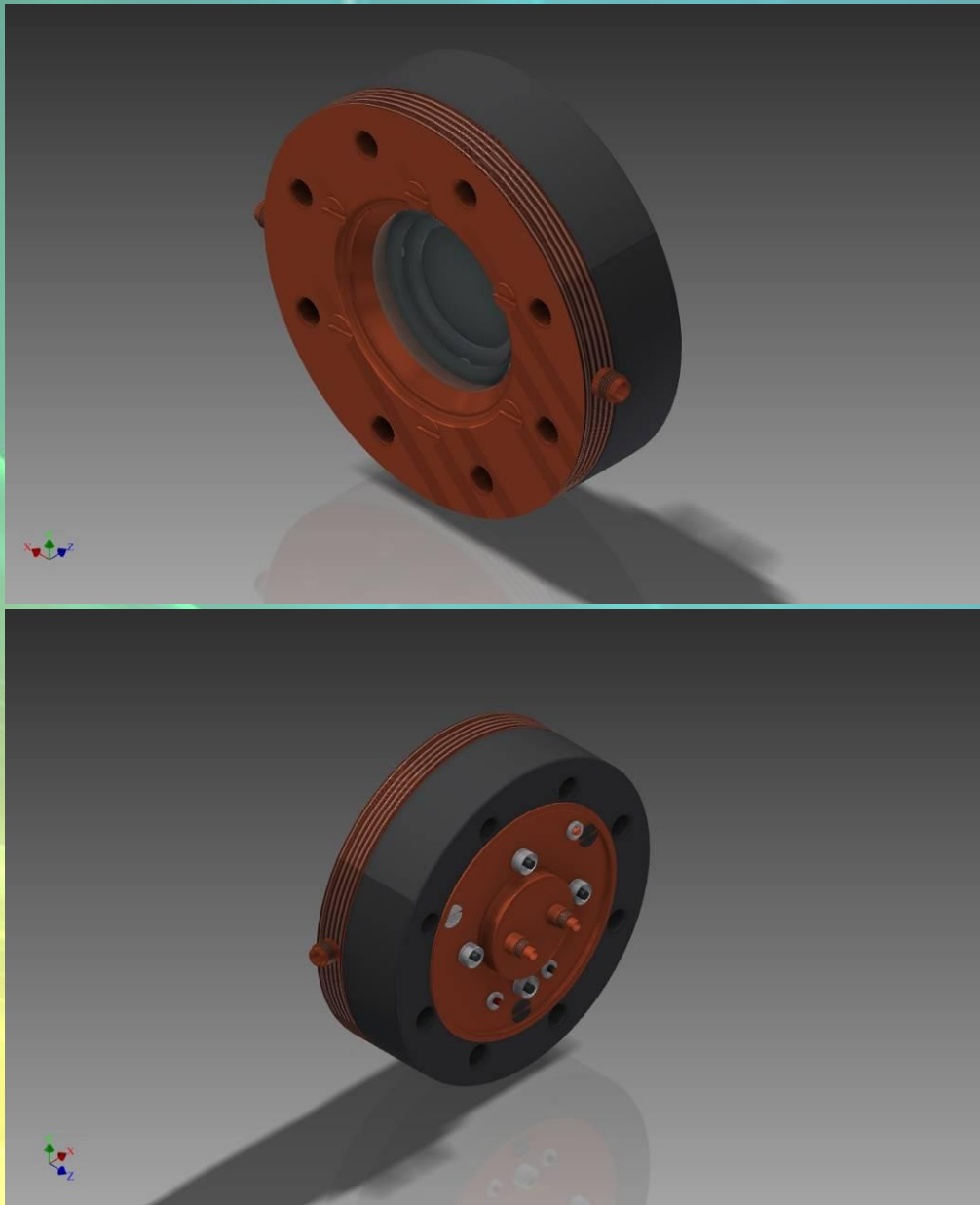
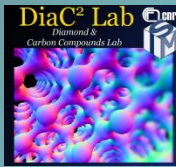
Enhanced Energy Production of Heat and Electricity by a Combined Solar Thermionic-Thermoelectric Unit System
EU FP7 Energy - Grant Agreement n. 241270

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The concept is an intellectual property of CNR (patent pending WO/2014/033690)

- High-temperature (up to 1000 °C)
- Maximum conversion efficiency >50% (6% now @ lab-level)
- Solid-state: no parts in movement - no degradation
- Scalable from small systems to solar towers





- **Compactness** (11.4 cm diameter × 4.0 cm thickness). The module has to be as compact as possible to reduce its volume for minimizing heat and optical losses and for reducing optical shadowing effects from non concentrated sun radiation;

- **Interchangeability of the components.** Each component can be mounted and dismantled thus favouring a strategy of continuous optimization of the CM performance;

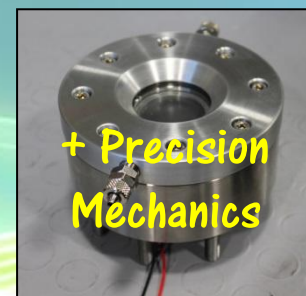
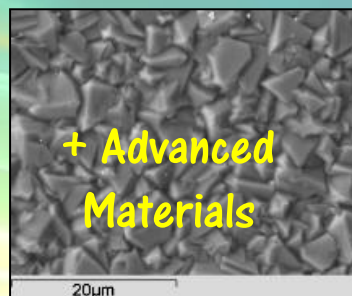
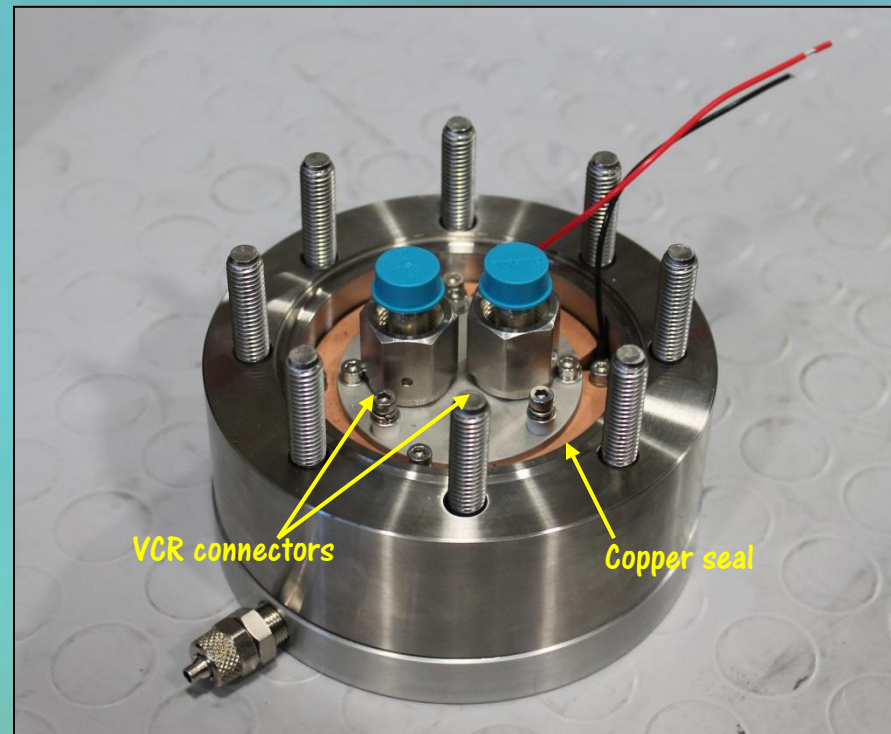
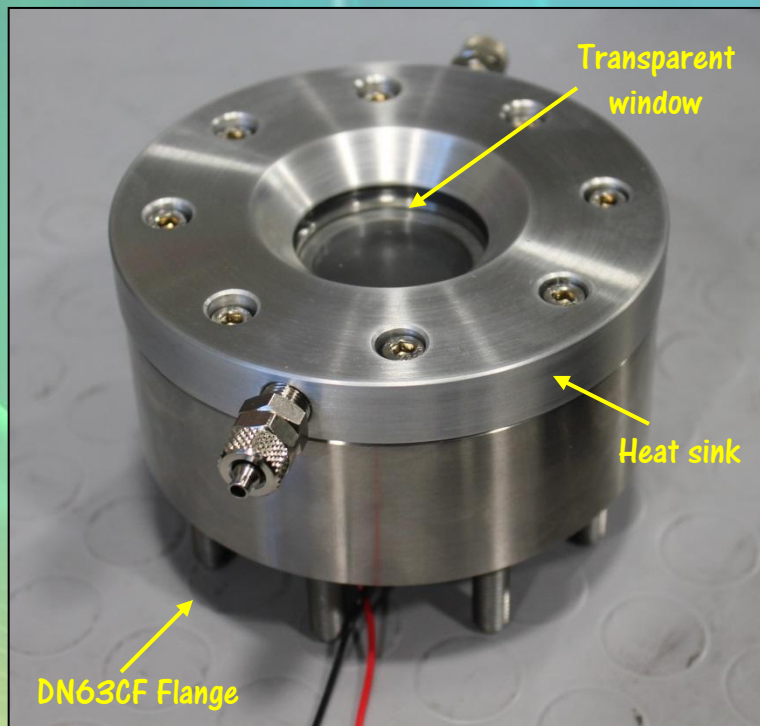
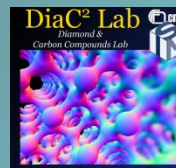
- **Mounting easiness.** The enclosure has been selected to satisfy commercial standards and takes advantage of this for mounting the module on its support;

- **Scalability.** The design is completely scalable at larger dimensions;

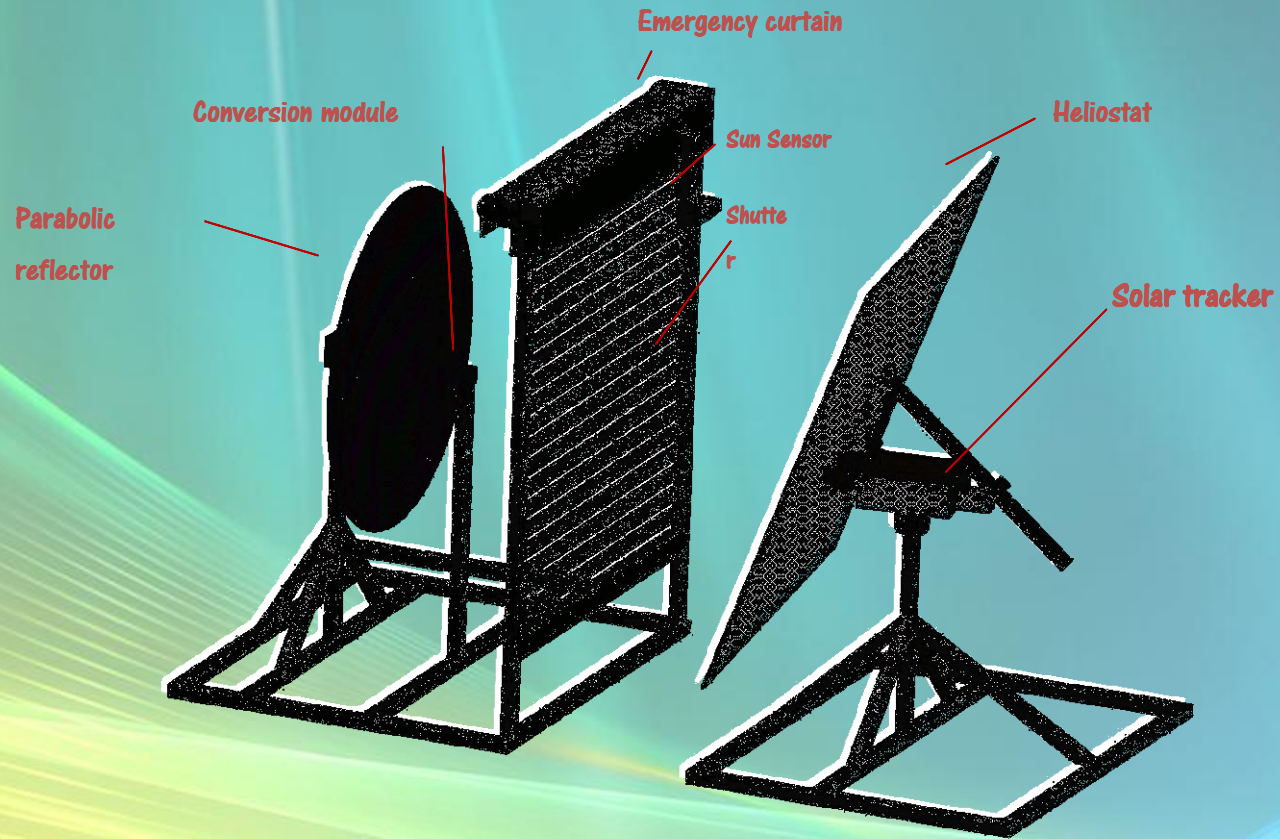
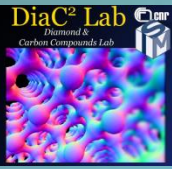
- **Robustness.** It has been studied a proper method to fix the active elements on the supporting flange and favour the collection of exhaust thermal fluxes in the primary thermal circuit.



Conversion Module - Enclosure Fabrication



Solar Test Platform (STP) - Design



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Solar Test Platform (STP)



1. the heliostat, the sun tracking system, built by assembling 8 rectangular flat mirrors
2. the parabolic concentrator with tile tessellation (3 cm x 3 cm)
3. the shutter system, appropriate for modulating the sunlight intensity
4. support for the conversion module

Concentration focus of 8 cm diameter, concentration ratio of about 200

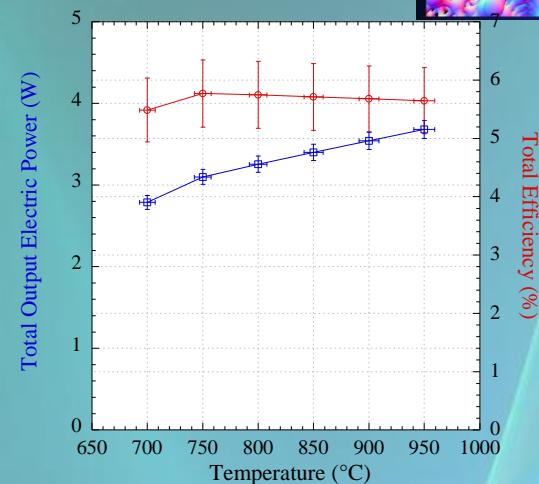
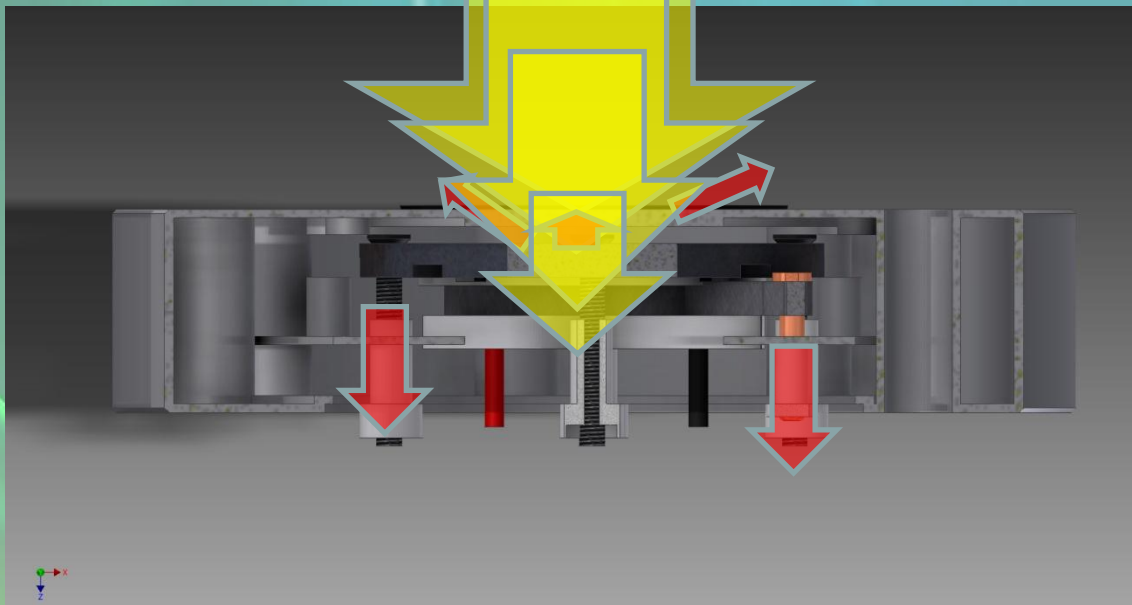
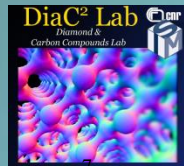




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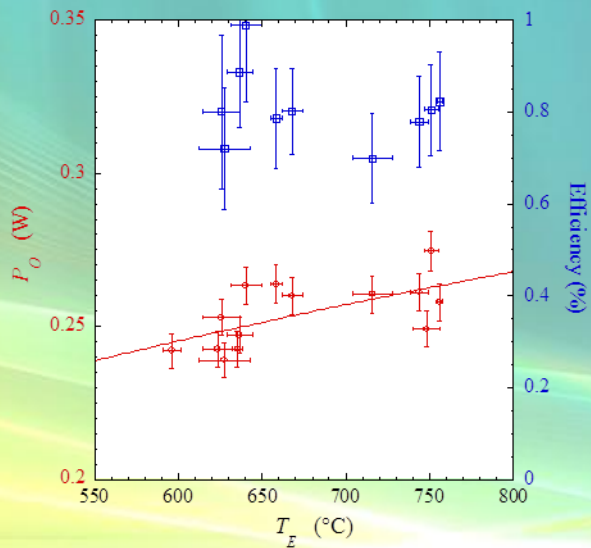


Conversion efficiency



Lab-Level:

Conversion efficiency close to 6%



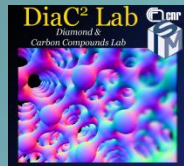
Under relevant conditions
 Conversion efficiency close to 1% +
 70% thermal efficiency
 Low value, but several improvements
 are possible

Proposed to the EU a prototype with a
 realistic 22% conversion efficiency
 with 3 year development

D.M. Trucchi et al., under finalization for Energy and Environmental Science



High-Temperature Solar Cells



PETE* devices can be defined as **optically transparent** **absorber** thin-film semiconductor with bandgap of 1.8 eV and a thickness of hundreds of nm **substrate** for mechanically **concentrating** cathode. Ideally, a number n semiconductor layers with **scaling bandgap** **Optimized d to allow photoelectron emission** in the following layer

of junction cells and **even benefit from high operating temperatures**

*J. Schwede, et al., Nature Materials 9 (2010) 762

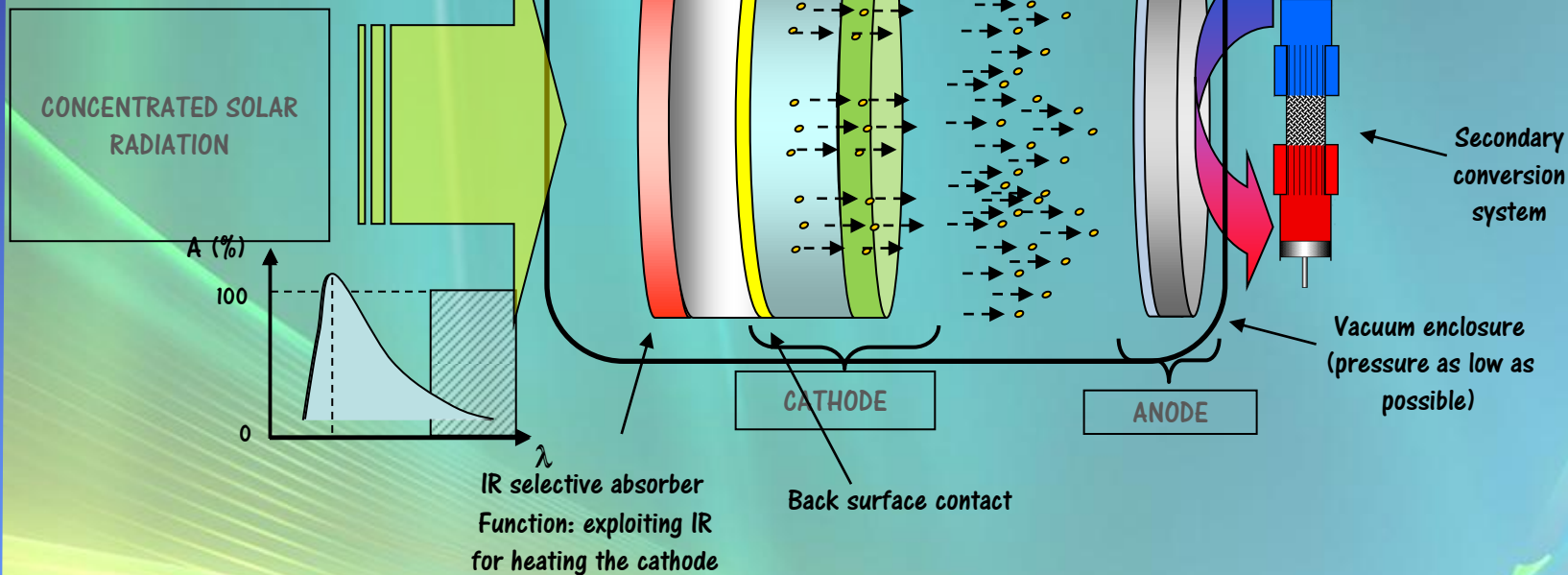


Photo-generation increases electron population at conduction band above the equilibrium level, and the emission energy barrier is reduced: more electrons are emitted from the cathode at lower cathode temperatures compared to conventional thermionic emitters

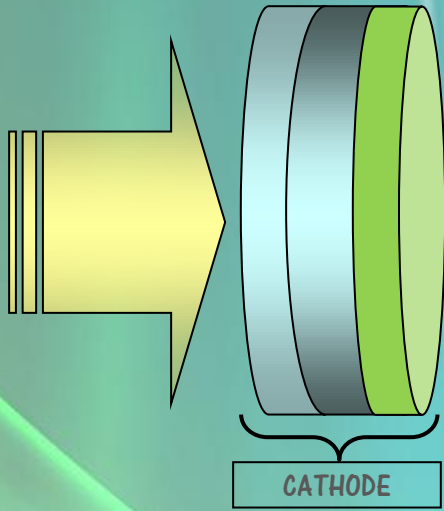
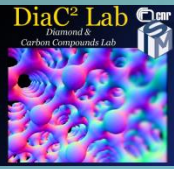
Thermalization processes within the cathode increase its temperature, further increasing the emission current density (thermionic emission)

PETE devices utilize both photonic and thermal processes for energy conversion, and are not subject to either the Shockley-Queisser limit or the thermal limit (Carnot)**

**G. Segev, Y. Rosenwaks, A. Kribus, Solar Energy Materials & Solar Cells 140 (2015) 464



Photo-Thermionic Cathode



- Advantage: no p-n junction is needed
- Capability to operate at high temperature
 - Exploitation of additional thermionic emission

III-V Semiconductors

Advanced IV Semiconductors
(CVD Diamond)

Advantages:

- Proper bandgap for absorption and photocarrier generation (about 1.8 eV)
- High electron diffusion lengths

Disadvantages:

- High work function -> Necessity of coatings for "work-function-engineering"
- Instability at high-temperature

Advantages:

- Low "native" work function caused by NEA conditions (surface hydrogen termination)
- Wide range of operating temperature (<780 °C)
- High thermal stability
- High robustness

Disadvantages:

- Wide bandgap (5.47 eV @ RT)

May 2013 - Apr 2016

Total Project Cost: 4.2 M€

Total EU Funding: 3.0 M€

www.prometheus-energy.eu

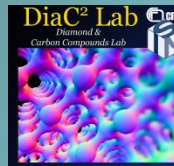


Bandgap Engineering

Defect Engineering



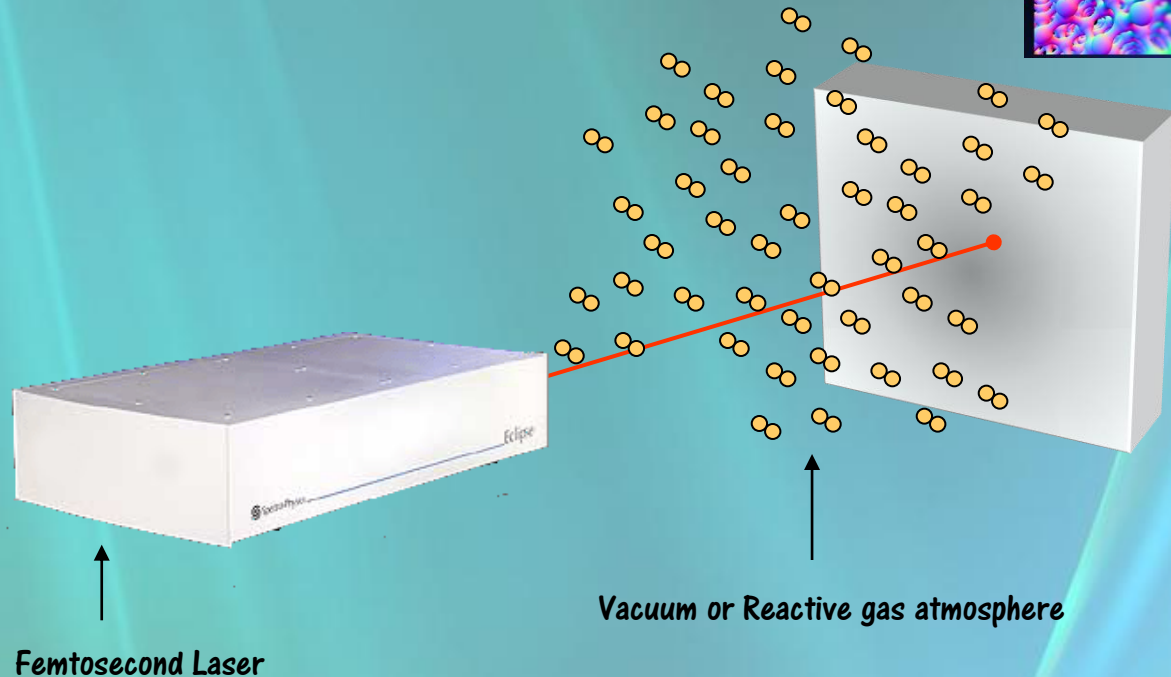
Surface Texturing - BLACK DIAMOND



Femtosecond laser pulses are able to texture the surface of materials and dielectrics with periodic nanoscale structures without use of photolithographic steps



Femtosecond Laser installed in the CNR-ISM of Tito Scalo (PZ)



Femtosecond Laser

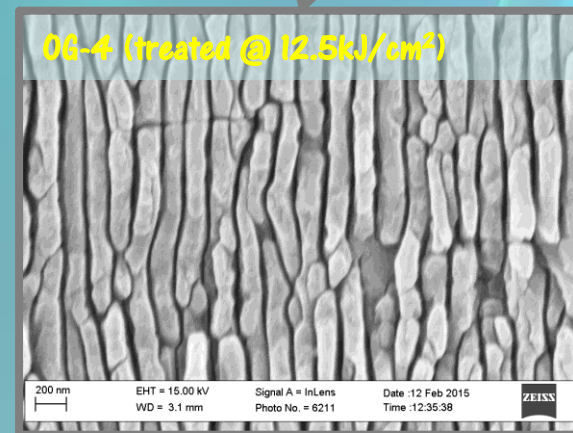
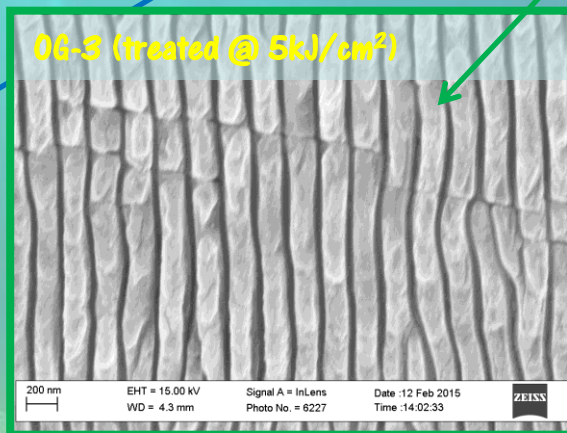
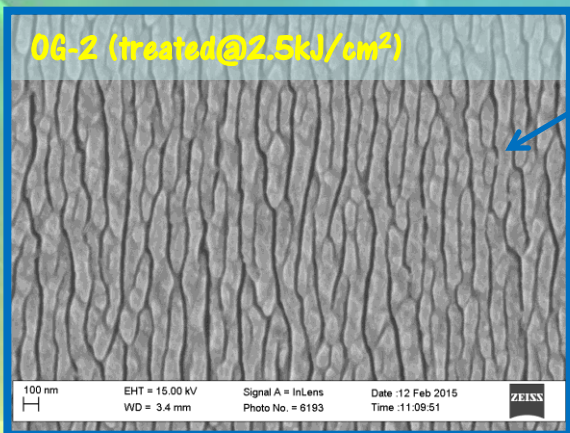
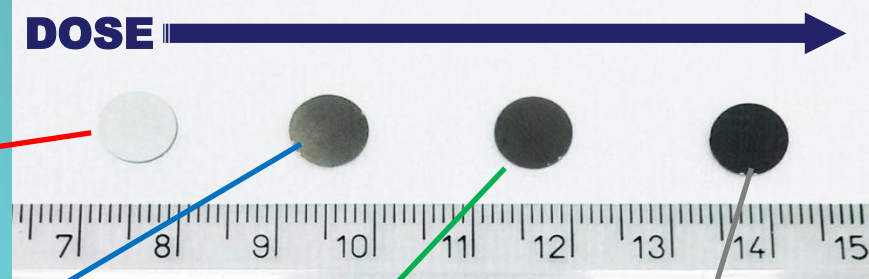
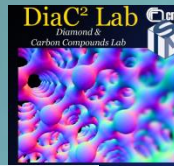
Vacuum or Reactive gas atmosphere



BLACK DIAMOND has advanced optical and electronic properties: it can be defined as a new material !!!



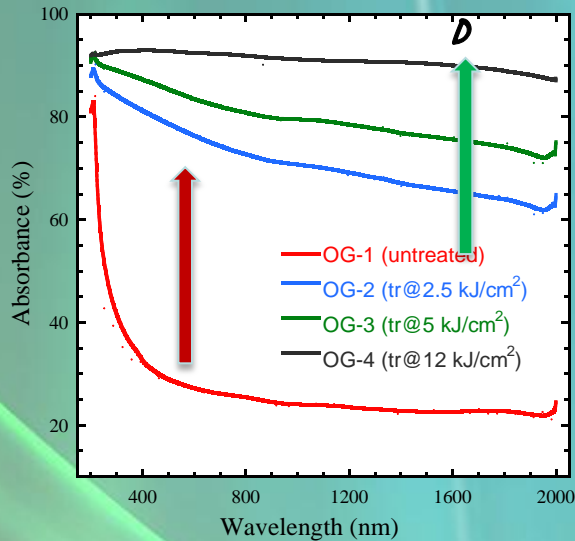
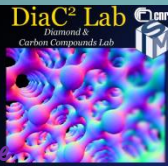
Surface Texturing - BLACK DIAMOND - Microstructure



- **Low doses (2.5 kJ/ cm²):** the structures are not well defined
- **Medium doses (5 kJ/ cm²):** defined linear structures with periodicity of 170 nm and length of several μ m
- **High doses (12.5 kJ/ cm²):** degraded structures (post-ablation)

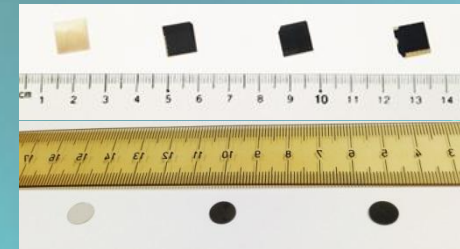


BLACK DIAMOND - Optical Characterization



Absorbance, reflectance, and transmittance spectra in the 200-2000 nm range highlighted:

- A significant increase in absorbance for the treated samples
- Absorbance is an increasing function of treatment dose D



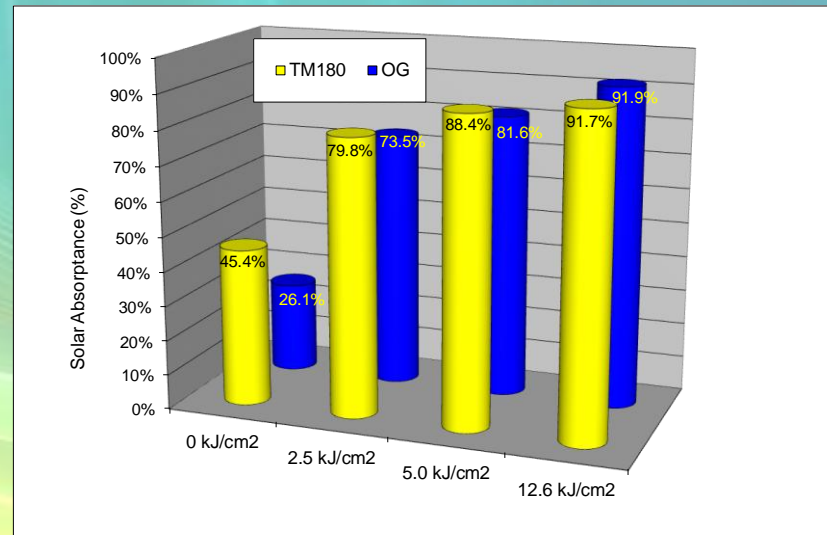
Optical Grade samples (OG)

Thermal Grade samples (TM)

The solar absorbance values are similar at a same treatment doses independently from the values of the untreated samples

- An efficient optical absorption is **ONLY** a **NECESSARY** but **NOT SUFFICIENT** condition for an efficient solar energy converter

- **ABSORBED PHOTONS** have to generate **CHARGE CARRIERS**

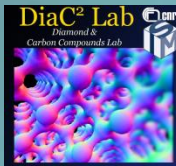


Solar absorbance α , defined as the normalized integral product between absorbance A and solar irradiance spectrum W_{solar}

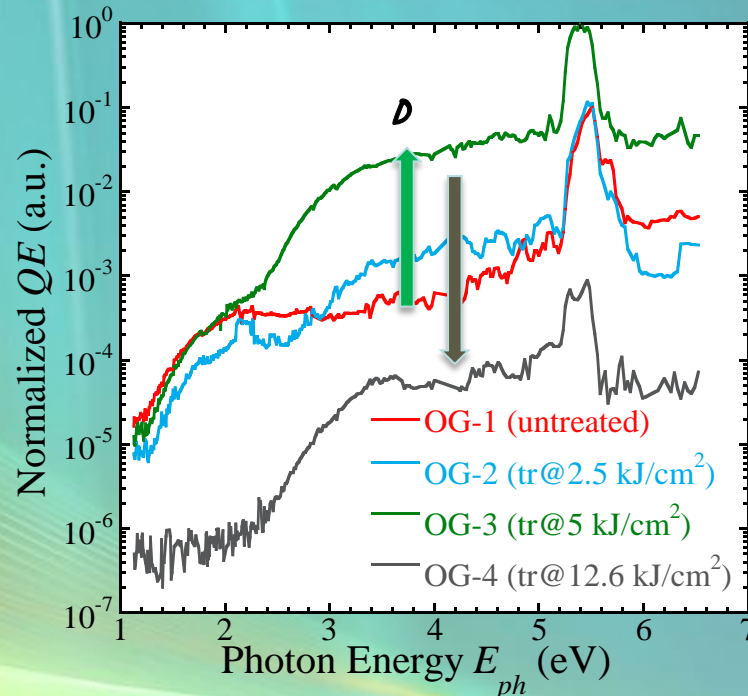
$$\alpha = \frac{\int_{\lambda=200nm}^{\lambda=2000nm} A(\lambda)W_{solar}(\lambda)d\lambda}{\int_{\lambda=200nm}^{\lambda=2000nm} W_{solar}(\lambda)d\lambda}$$



BLACK DIAMOND - Photo-Electrical Characterization



Spectral photoconductivity measurements have been performed to quantify the photogeneration capability of useful charge carriers



$$\text{Quantum Efficiency } QE = R(h\nu) \frac{h\nu}{q} = \frac{\text{electrons} / \text{s}}{\text{photons} / \text{s}}$$

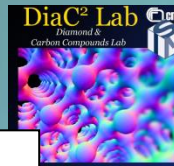
- The external *QE* of the most performing sample is maximum at bandgap energy. *QE* ranges from 2% to 6% from about 3 eV (\cong 420 nm) to 5.1 eV (\cong 250 nm)
- This is an excellent result, but needs to be further improved for competitive performance with solar radiation

A. Bellucci, P. Calvani, M. Girolami, S. Orlando, V. Valentini, R. Polini, and D.M. Trucchi , in preparation

Tito Scalo, January 20th, 2016 - OSCAR Final Workshop



BLACK DIAMOND - Origin of the effect



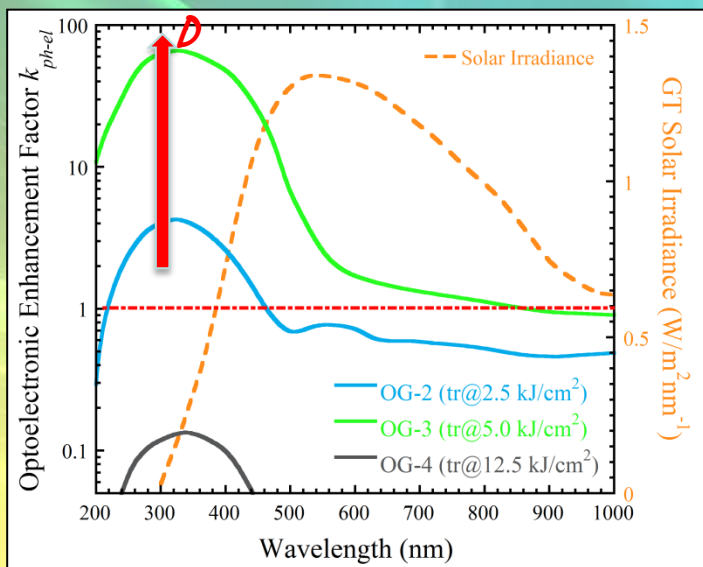
In order to disentangle the effect of:

- absorption centers and
- electronically defect states

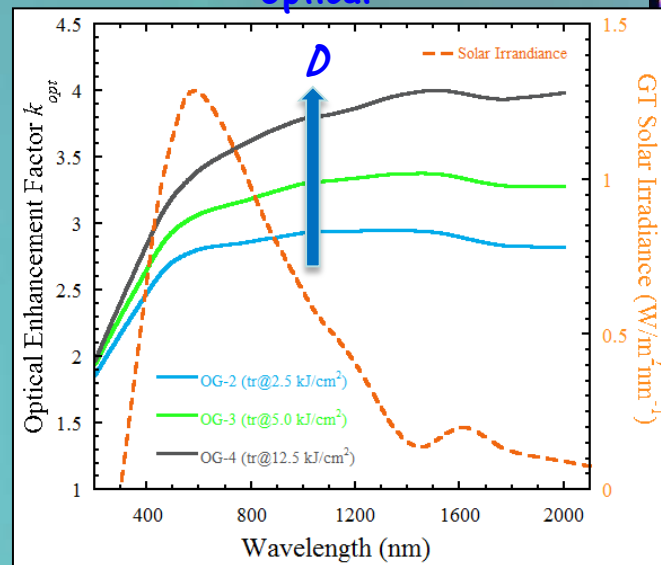
natively present in the crystal from the ones induced by the periodic surface texturing, we define

$$k_{opt}(\lambda) = \frac{A_{treated}(\lambda)}{A_{untreated}(\lambda)} \quad k_{pe}(\lambda) = \frac{QE_{treated}(\lambda)}{QE_{untreated}(\lambda)}$$

Photoelectric



Optical



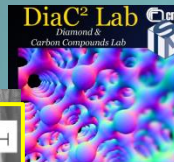
The trends of the two parameters are different:

- k_{opt} is an increasing function of λ : it shows a sharper slope up to 500 nm, to finally reach an almost constant value (3 ÷ 4) for longer wavelengths
- k_{pe} is composed by broad peaks due to the introduction of shallow traps (down to 2.4 eV from extended bands), which:
 - A) induce a photocurrent increase far larger than the pure optical amplification at shorter wavelengths
 - B) Are ineffective for wavelengths longer than 800 nm (where the optical enhancement is close to the maximum value)

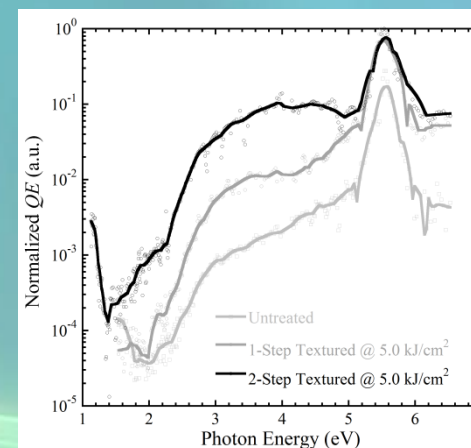
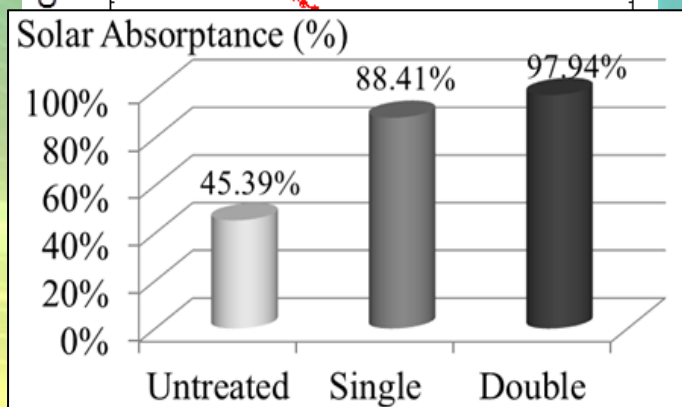
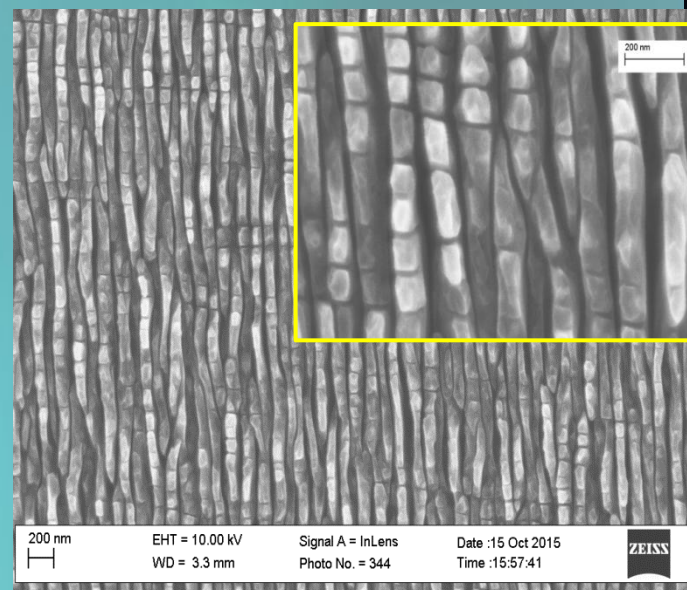
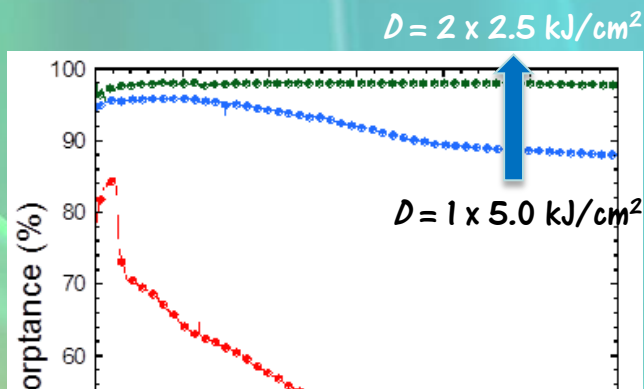
We suppose that the subwavelength surface texturing acts
Optically as a diffraction grating smoothing the refractive index of the material
Electronically by introducing an intermediate band favoring the photogeneration



BLACK DIAMOND - Attempts for a 2D periodic texturing

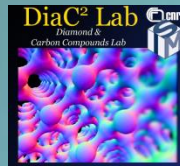


- Treatment at $D/2 = 2.5 \text{ kJ/cm}^2$
- Sample rotation of 90 deg around the direction perpendicular to the laser beam optical path
- Treatment at $D/2 = 2.5 \text{ kJ/cm}^2$

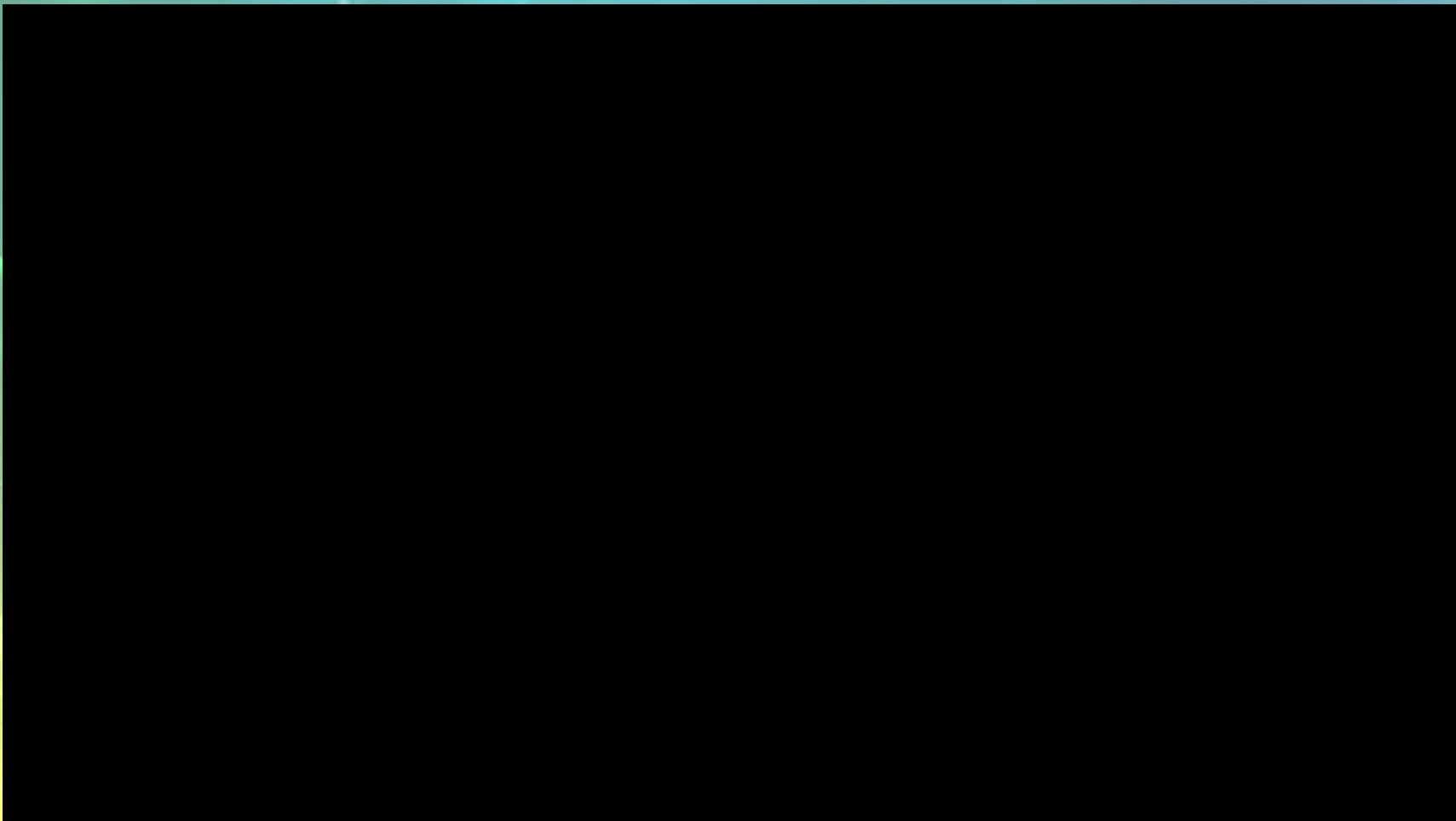


Responsivity increases of a further order of magnitude at each sub-bandgap wavelength up to 700 nm





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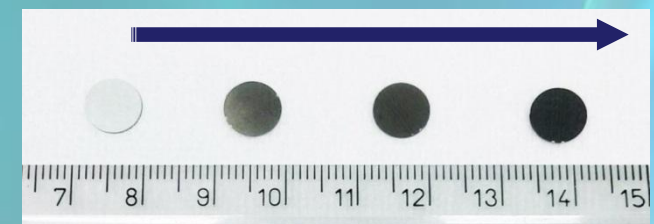


Tito Scalo, January 20th, 2016 - OSCAR Final Workshop



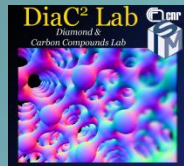
KETs {

Nanotechnologies
+
Advanced manufacturing techniques
+
Advanced materials
+
Know-how
=

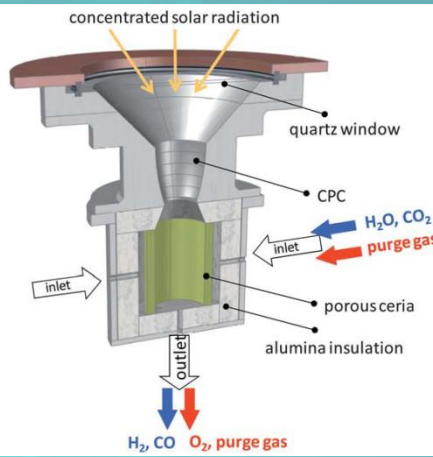
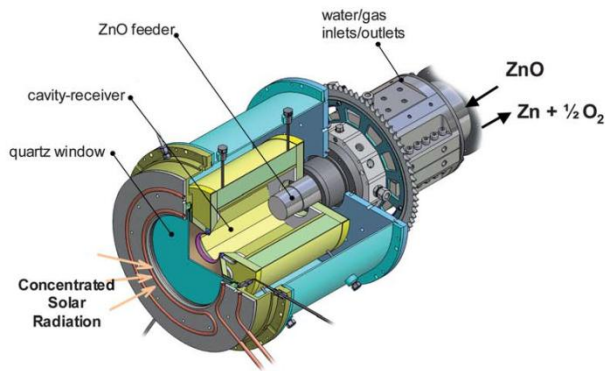


**International competitiveness of
new added-value high-tech products**

Complementary Technologies



Energy Environ. Sci., 2012, 5, 9234



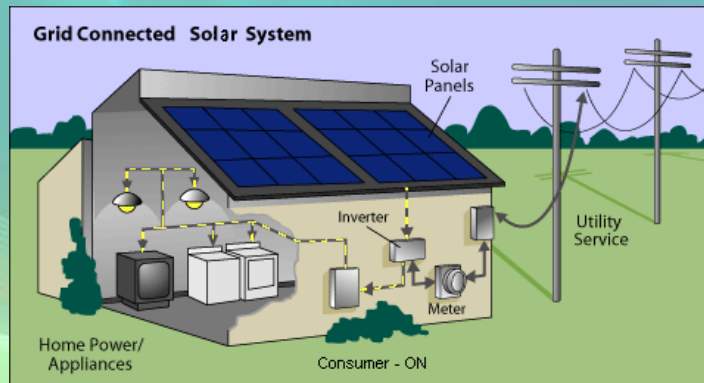
Chemical reactors for production of solar fuels (hydrogen, oxygen, carbon dioxide, etc.)

Predictive and adaptive solar tracking



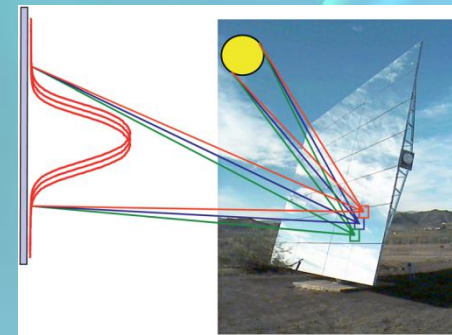
Solar tracking is an established technology BUT based only on geographical parameters (latitude, altitude,) and not on real-time weather measurements

Transformation and transport of energy



High-efficiency electronic devices: inverters, step-up DC-DC converters, high-power diodes and transistors

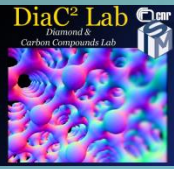
Concentrating Optics



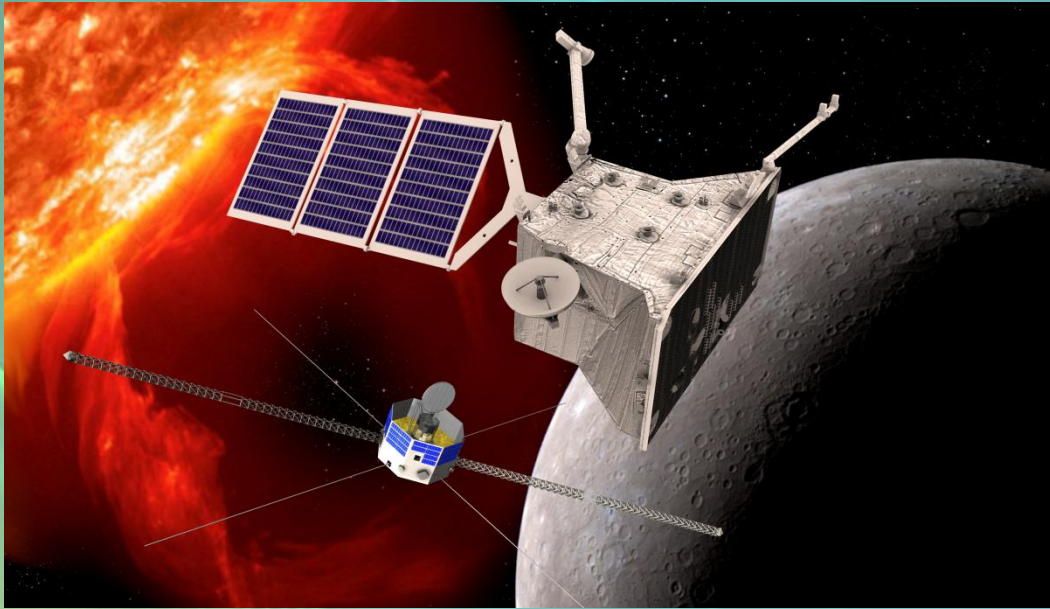
Lower cost, higher reflectance, possible dichromatic properties



Other Applications



Aerospace



ESA Bepi Colombo Mission to Mercury
Light Intensity = 10.6 suns

Industrial

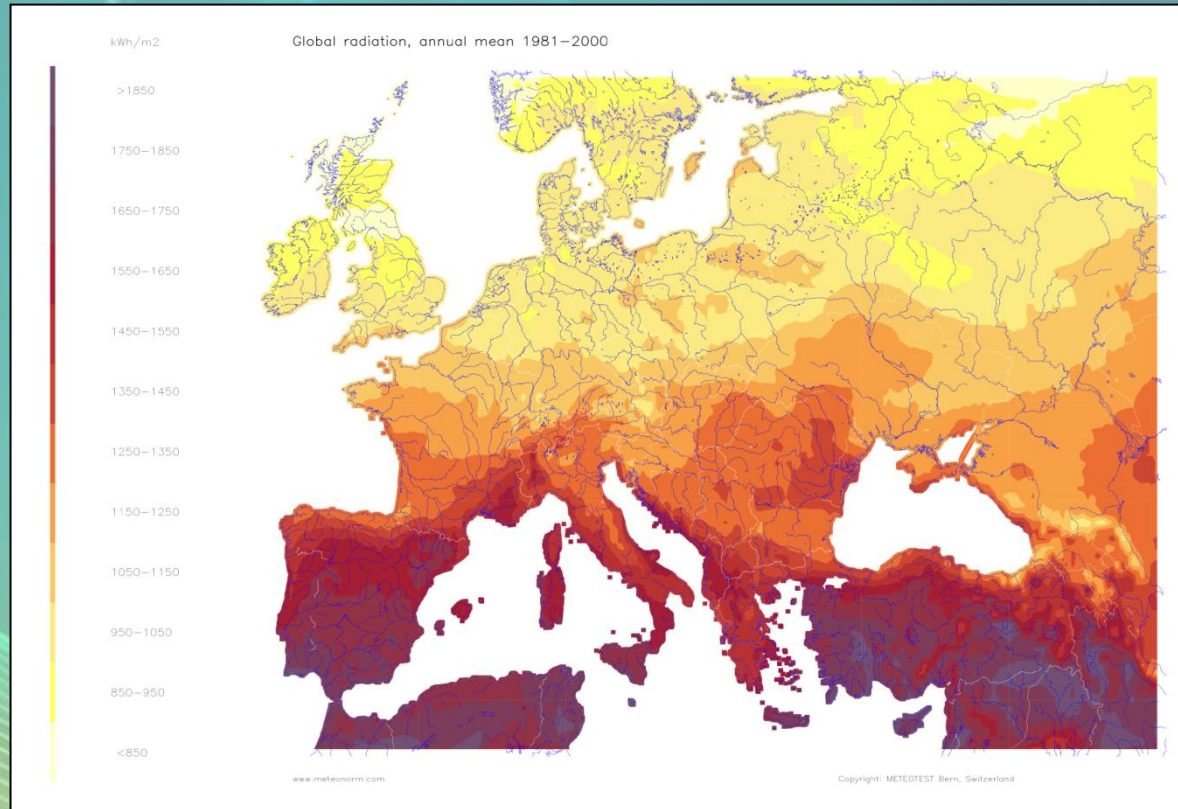
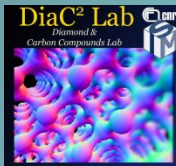


Heat recovery from
high-temperature
reactors

Geothermal
(high enthalpy systems)



Conclusions



CNR proprietary innovative technologies are continuously under development as enabling solar technologies

They can be combined to integrated complementary technologies covering several know-hows

Their application can be also in other interesting fields



Thank you for the Attention!

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