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PROJECT FINAL REPORT

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Project title: **Production Method of Electrical Energy by Enhanced Thermal Electron Emission by the Use of Superior Semiconductors**

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1. Executive summary

The objectives of the FET project ProME^{3}ThE^{2}US^2 were the development, validation, and implementation of novel solid-state structures able to convert directly concentrated solar radiation into electric energy at very high efficiencies. The proposed innovative structures are based on the exploitation of photon-enhanced thermionic emission (PETE) mechanism.

The advantages of the PETE devices are connected to the capability to overcome the limitations of traditional solar cells (even the more advanced multiple junction ones) when operating in solar concentrating systems. The characteristics of PETE converters are indeed a better operation at increasing operating temperatures and a more efficient use of the solar photons by exploiting, along with the direct photogeneration of charge carriers in a semiconducting absorber, all thermalization effects and IR absorption as useful heat sources for thermionic emission. PETE operates through a cathode able to emit both photogenerated and thermionic electrons. The device is completed by an anode able to receive the emitted electrons and transfer them to a load for the exploitation of the converted electric power by enabling a current flow. For their thermal operational ability, PETE converters can be defined as "high-temperature solar cells".

In ProME^{3}ThE^{2}US^2 project, eight partners, spanning from a University to three applied research centres, from three SMEs to a big company, worked for developing novel technologies for PETE devices, some of them applicable also to general thermionic energy converters.

Three different cathode technologies were developed according to different design strategies: *bandgap* and *defect engineering*:

1) **III-V phosphide** structures (GaInP) were designed and fabricated for defining a device able to absorb efficiently the sunlight thanks to a *tailoring of the bandgap* to the optimal value of 1.8 eV, completed by back surface and emitting surface barrier layers, as well as optimized electric contacts and coatings for electron affinity reduction.

2) Concurrently, the first *defect-engineered* diamond cathode was designed and fabricated. This technology merges together a novel material – the "black diamond"– and advanced techniques for 3D graphitization and diamond doping in order to reduce series resistance and increase emission capabilities. The black diamond, namely a surface-nanotextured **single-crystal or large polycrystalline diamond film**, is by itself a significant result, being a novel material with surprising physical properties: exceptional capability to absorb sunlight (>90%), strongly enhanced photoelectronic generation, and improved charge transport if compared to the pristine crystal.

3) The *defect engineering* strategy did not follow only the route of introducing defined defects in high quality crystals, but also of controlling a large amount of defects in **small-grain polycrystalline diamond films**. This is the case of diamond membranes, namely diamond films with a thickness of few micrometres and supported by a silicon frame.

A dedicated brand new technology based on dielectric inter-electrode microspacers, that can be transferred to all the thermionic emission active devices, was developed. Stoichiometric alumina microstructures were directly produced on the anode surface to establish a micrometric distance between the thermionic electrodes (1.5 μm), potentially able to neutralize the space charge effects.

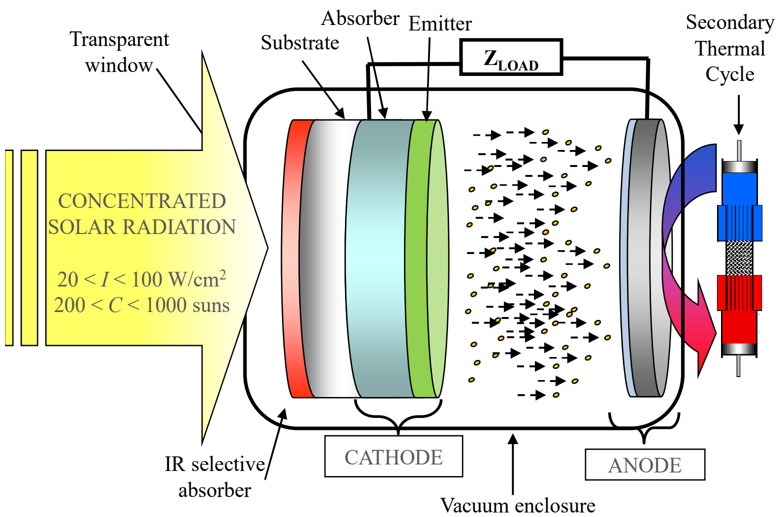
Black diamond and GaInP cathodes were tested with a dedicated and versatile experimental setup, designed, fabricated, and assembled in combination with a high-flux solar simulator for the first characterization of PETE components under realistic conditions. Surprisingly black diamond cathodes, even still far from a definite optimization, showed better performance in terms of emission current than the III-V structures, with these probably limited by not completely optimized emitting surface properties.

2. Summary description of project context and objectives.

The ProME^{3}ThE^{2}US^2 project - *Production Method of Electrical Energy by Enhanced Thermal Electron Emission by the Use of Superior Semiconductors* - aimed at developing, validating, and implementing novel solid-state structures able to convert directly concentrated solar radiation into electric energy at a very high efficiency. The objective of the project was the development of efficient high-temperature solar cells, based on engineered semiconductors, able to overcome the limitations of multiple-junction cells. ProME^{3}ThE^{2}US^2 is a European collaborative project within the Energy FP7 framework of Future Emerging Technologies (FET). Coherently with the FET strategy based on high-risk research, the project aims at incubating and developing a breakthrough concept for direct conversion of concentrated solar radiation, with a very high technological impact.

The core conversion mechanism is enhanced electron emission. The cathode, based on advanced semiconductor structures, operates as a photo- as well as a thermionic-cathode (PETE – Photo-Enhanced Thermionic Emission device, firstly demonstrated by Stanford University), taking advantage of the high temperature achieved from the absorption of the IR part of solar radiation (not able by itself to photo-induce charge carrier production), and from thermalization of hot electrons, i.e. electrons directly generated by higher-energy solar photons.

The solid-state converter operates under vacuum conditions to allow emitted electrons to travel from the cathode to the anode. Although vacuum conditions could be considered as a technological complication, on the other hand they allow for a substantial reduction of heat losses. The solar radiation, with a concentration ratio roughly ranging from 200 (but also 50 could be sufficient) to 1000 suns (typical of point-focus systems), impinges on the converter through a transparent window. The engineered cathode is mechanically supported by a transparent substrate. An optional IR spectrum absorber is deposited on one of the surfaces of the substrate, aimed at transforming into heat the energy of IR photons, not able to induce direct photogeneration. The solar absorber is a thin-film semiconductor (thickness of hundreds of nanometres) deposited on the second surface of the transparent substrate, and has the function to capture most part of the solar spectrum, converting it into charge carriers. By designing a proper band structure, electrons can be injected into the last thin coating characterized by a low work function to allow electrons to escape efficiently into vacuum. Emitted electrons have to travel in vacuum for a micrometric distance, small enough to avoid space charge effects: to satisfy this condition, an innovative micromachining technology for obtaining dielectric microspacers is developed. Emitted electrons are finally collected by an anode consisting of a substrate (usually metal, to decrease the converter series resistance) coated by a film with a work function lower than the cathode one (this is a condition to achieve a steady-state current with no bottlenecks). The exhaust heat on the anode, mainly produced by the thermal irradiance of the cathode, can feed a secondary thermal cycle of conversion, that can be based (but not limited to) on the use of thermomechanical engines. In other words, the PETE device can act as a topping cycle for additional conversion stages, with a total efficiency resulting in a linear combination of the efficiencies of each stage.



The efficiency of the solid-state device, analysed by advanced simulation methods and performed by the groups of the Tel Aviv University involved in the project, can be as high as 52% at a concentration ratio of 1000 suns. Combined to a secondary thermal cycle, the system efficiency limit increases up to the outstanding value of about 70%, higher than the Carnot and Shockley–Queisser limits [1]. The system may be co-generative, thus supplying additional exhaust thermal energy as an output for the needs of future end-users (domestic and rural applications).

The main project objective is to set the basis of each technological step, excluding the secondary thermal cycle, which, being a consolidated technology, is analysed through comparative simulations, performed by Exergy on different solutions present on the market.

The specific project objectives are:

1. Development of efficient PETE cathodes;
2. Development of an engineered anode with physical properties matched to those of the cathode;
3. Development of dielectric microspacers able to reduce space charge effects and minimize the thermal flow between the converter electrodes;
4. Development of advanced simulation methods with a continuous refinement related to the feedback from experimental activities;
5. An enhanced knowledge of the physical properties of semiconductors and related structures at high temperature conditions, which represent conditions hardly analysed by the scientific/technological literature, and may pave the way to new applications.
6. Testing and demonstration of the proof-of-concept.

3. Description of the main S&T results/foregrounds.

In the following, the main project results are reported.

3.1. Development of efficient PETE cathodes.

The development of the cathodes has led to the production of three different technologies:

a) III-V phosphide cathodes. The structures are based on a bandgap engineering of the active absorber obtained by developing semiconductors with a bandgap matched to the solar spectrum. Fraunhofer ISE developed engineered GaInP cathodes, the layers of which are developed by MOVPE (Metal-Organic Vapor-Phase Epitaxy) and are characterized by high levels of crystallinity and large electron diffusion length. Phosphide cathodes were successfully produced by transferring the multilayer structures from the GaAs growth substrate to transparent sapphire wafers by means of the novel technology of surface activated wafer bonding.

Fig. 1. Evolution of the three cathode generations.

Three generations of cathode structures (Fig. 1) were designed and developed according to a guiding feedback from the simulation activities:

- *First generation*. The electric contacts are situated laterally on a highly doped conduction layer, and make electrons flowing in the structure along all the active volume, from the directly illuminated side to the emitting one. Lateral conduction layers lead to parasitic absorption of photons, reducing conversion efficiency: this issue was addressed by 2nd and 3rd cathode generations.

- *Second generation*. The contacts are not lateral, but directly situated on the emitting surface. This technological solution reduces the available emission surface, conversely it enables a more efficient drain of electrons from the absorber than the 1st generation. Indeed, this solution reduces device resistance and ohmic losses, not only for the positioning of refilling electrodes on the emitting surface but also for a possibly larger contact grid. The contacts can also be used to enhance the optical performance of the structure, either by absorbing sub-bandgap radiation (IR coupling) or by increasing photon recycling within the cell (back reflector). Optimal surface coverage values were estimated to be <30% of the emitting surface.
- *Third generation*. The third generation differentiates from the second one for a highly p-doped GaAs layer interposed between the electric contact and the affinity layer to reduce the contact resistance. Moreover, the barrier height of the back surface field layer was increased by the use of p-AlInP with a bandgap of about 2.2 eV, aimed at avoiding carrier leakage. Further improvements include optimization of the potential barrier height of AlGaInP layers, as well as a metal grid structure to ensure proper distribution of the current. Finally, the cathodes are coated on the sapphire side with a TaOx/MgF_2 bilayer anti-reflection coating to minimize reflection of sunlight.

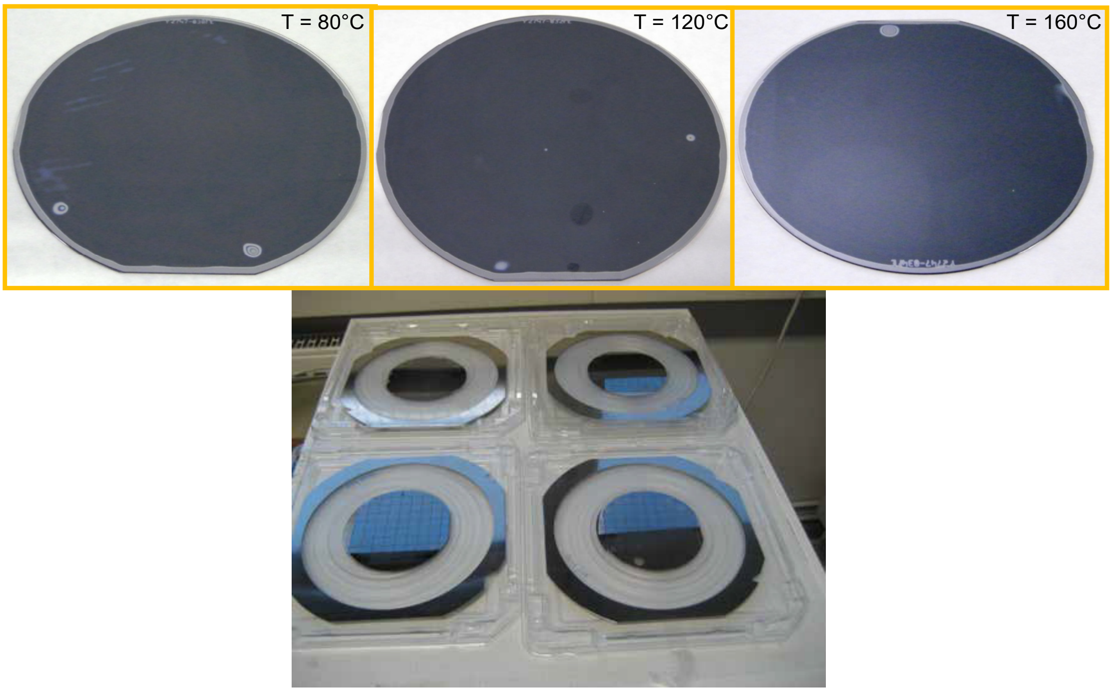


Fig. 2. a) III-V phosphide structures after wafer bonding at temperatures ranging from 80 to 120 °C. Some defects due to the process are evident on the wafer surface. b) Second generation wafers divided in sectors, hosting 1×1 cm^2 cathodes and test structures.

All the three configurations have GaInP absorbers developed with suitable bandgap energy of 1.8 eV at room temperature, as well as barrier layers for the absorber, contact layers and other functional components of the cathode (Fig. 2). Titanium electric contacts were selected among Au, Ag, WC conductors since experimentation demonstrated that they have an ohmic behaviour at temperatures up to 300 °C.

III-V semiconductors do not natively show a low work-function, that represents the primary property for an efficient cathode. They need for an additional very thin coating (atomic monolayer or even less) of a material characterized by a low work-function to allow electrons at the interface to be efficiently emitted into vacuum. The materials developed within the project are alkali-based coatings of Ba and

BaO, potentially thermally resistant. The obtained quality of these films, owing to the limitations of the "*ex-situ*" deposition (i.e. deposition of the coatings under vacuum or inert gas conditions followed by exposure to air), are debated and needs further research activity, even though a strategy of development was defined within the project activities by Solaris Photonics Ltd. The main issue is the agglomeration of the composites into "islands" when exposed to air, causing a non-homogeneous coverage on the cathode surface (Fig. 3).

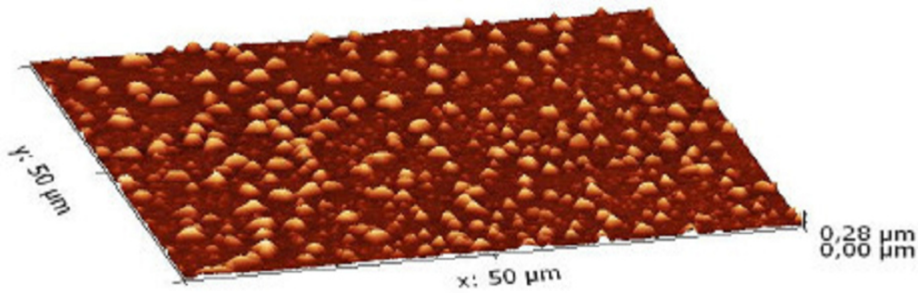


Fig. 3. AFM micrograph showing the typical "island" structure of Ba and BaO films exposed to air conditions.

The electronic properties of the GaInP-based structures were accurately characterized by time-resolved photoluminescence in terms of electron lifetime in the semiconductor bulk (i.e. the parameter indicating how an electron can travel within a crystal before recombination) and surface recombination velocity (i.e. the parameter indicating how much electrons can "survive" on the surface before their possible emission). Fig. 4 reports results on the initial structures: it is worth noting that lifetime (Fig. 4a) increases with temperature as expected from the increasing mobility, but there is also a dramatic increase in surface recombination velocity (Fig. 4b), due to a leakage of carriers at temperatures larger than room one, that could hamper the device performance in operating conditions.

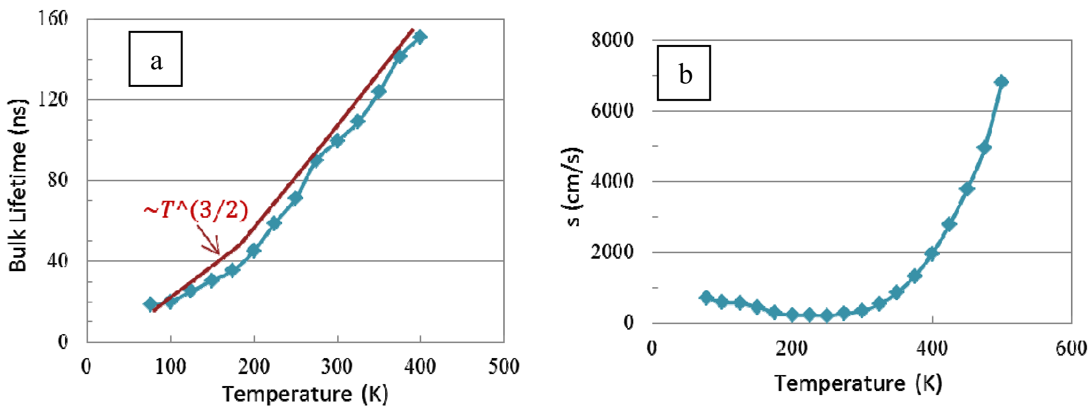


Fig. 4. Dependence as a function of temperature of a) electron lifetime in the bulk and b) surface recombination velocity.

Bulk lifetime showed an increasing behaviour with the potential barrier height of the final layers (i.e. the layers before the electron affinity coating). At 300 K, lifetime saturates over a certain barrier height value (Fig. 5a), whereas at 500 K saturation was not observed (probably occurring at even higher temperatures), and the curve is more scattered. These results were proficiently used to tailor the barrier height of the final layers to improve bulk lifetime.

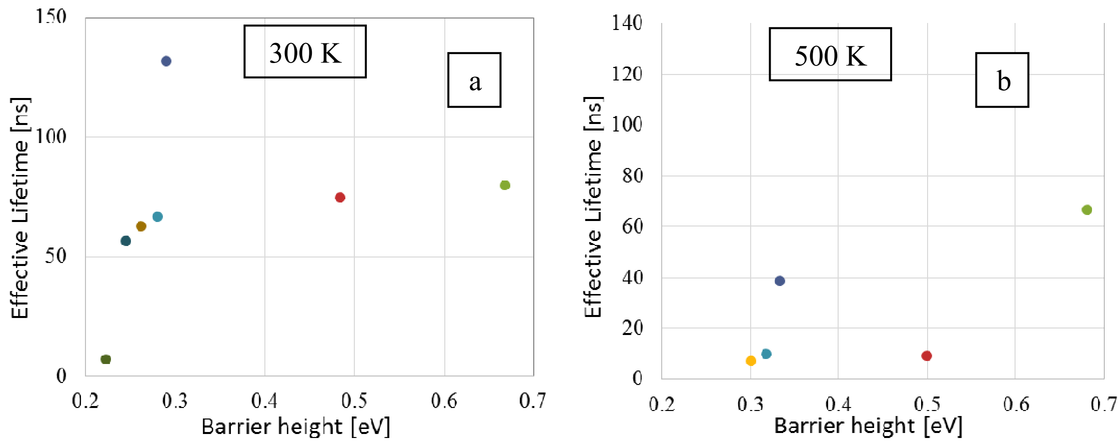


Fig. 5. Carrier effective lifetime as a function of the barrier height in the last structure layer at a) 300 K and b) 500 K.

The optimized structures were indeed found to have a very high bulk lifetime, with a maximum around room temperature (about 400 ns), after that a decreasing trend is visible (Fig. 6a). At 500 K the absolute values are still high enough (few tens of ns) for the application, but a clear temperature limitation for the device performance can be expected for temperatures > 600 K. On the other hand, the optimization of the final barrier height before emission induced an almost constant dependence of recombination velocity on temperature (Fig. 6b), thus pointing out the emission capability of electrons staying on the semiconductor surface.

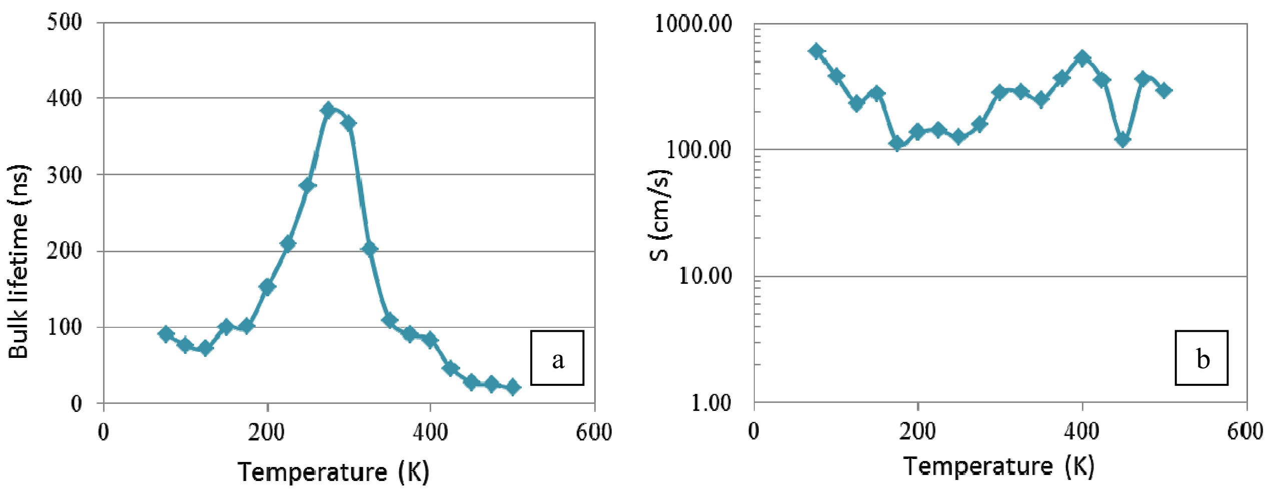


Fig. 6. Dependence as a function of temperature of a) electron lifetime in the bulk and b) surface recombination velocity in the third generation cathodes.

b) Black diamond cathodes. The second technology is based on a *defect engineering* performed on high crystalline quality wide-bandgap CVD (*chemical vapour deposition*) diamond films and is developed by Consiglio Nazionale delle Ricerche (CNR). Diamond work function can be significantly reduced by hydrogenating its surface. Hydrogen atoms induce a strong negative electron affinity, making diamond a candidate for an efficient thermionic cathode material. Hydrogen-carbon bond is very stable up to temperature of 780 °C, giving a high operational robustness to the diamond cathode. Therefore, electrons are able to easily escape from diamond surface into vacuum. Conversely, diamond has a wide bandgap, correlated to a high transparency to the solar light, so it does not nominally absorb the solar radiation.

A novel material, **black diamond**, was prepared in the project to attribute diamond additional capabilities [2]. Black diamond is able to optically absorb the solar radiation up to values >90% [3-4] and it has electronic states in the bandgap able to interact with solar photons, as well as to increase dramatically the photo-electronic capability [5]. Black diamond films (Fig. 7) were obtained by a surface nano-texturing produced with the use of ultrashort (fs) laser pulses.

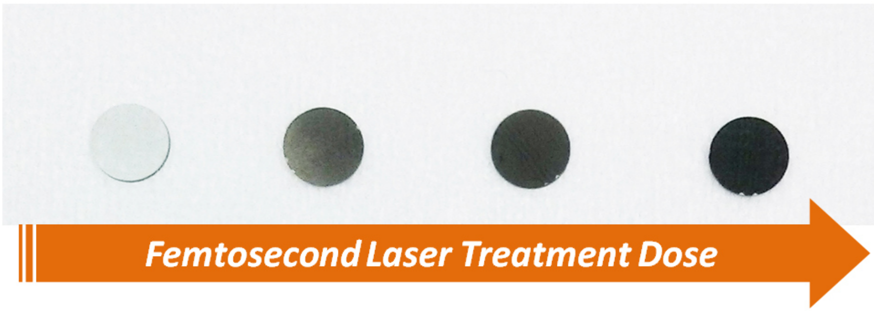


Fig. 7. Diamond films become black diamond films by acting on laser treatment dose.

The optical and electronic dominating effect is correlated to the surface texturing, characterized by a nanoscale periodicity (the process optimized parameters presently indicate a period of 170 nm, obtained for a laser accumulated dose of 5.0 kJ/cm^2 – Fig. 8).

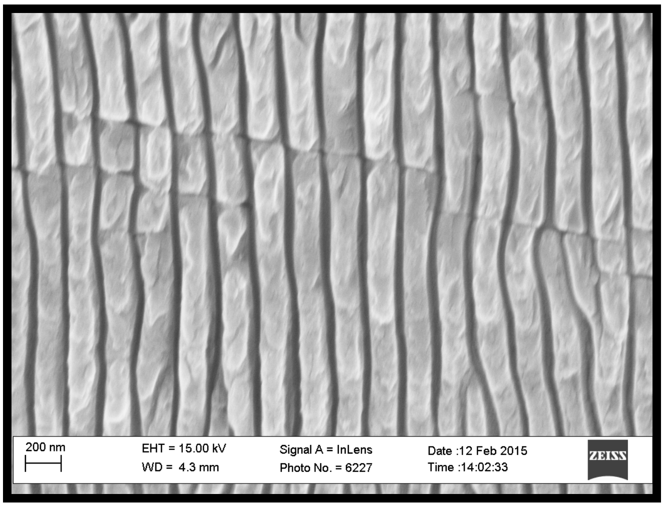


Fig. 8. 1D periodic (170 nm period) microstructure of black diamond surface.

Like doping, introducing point defects in a periodic lattice, surface periodic defects act electronically within the diamond bandgap by introducing energy levels that can be useful or detrimental for the crystal photo-electronic properties, depending on their position with respect the extended bands. The present and future core development activities are indeed focused on a better control of defects behaviour by finely tuning the shape, depth, periodicity, of 1D or 2D structures.

About the possibility of fabricating a 2D periodic texturing, attempts were made towards this direction by means of a 2-step treatment [6] at the optimal accumulated laser dose (Fig. 9).

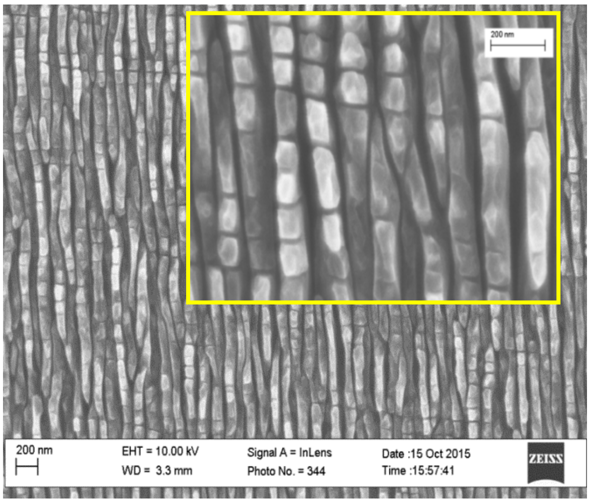


Fig. 9. Attempt for a 2D periodic microstructure. Even if the periodicity and definition is imperfect, the electronic and optical results suggested the validity of this strategy.

Although imperfect structures were obtained, the resulting solar absorptance was measured to be equal to 97.9%, a value very close to 100% (Fig. 10), and a further enhanced photoelectronic capability was achieved, thus demonstrating the effectiveness of the transition from 1D to 2D periodic structuring.

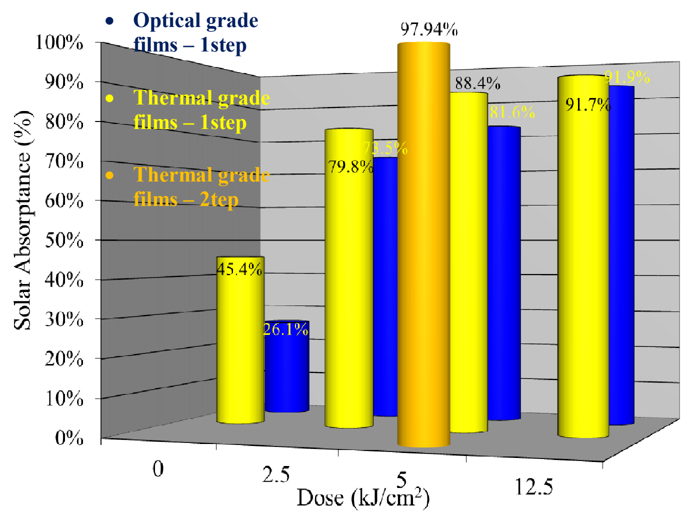


Fig. 10. Solar absorptance of diamond film sets as a function of treatment dose. The optimal dose was found to be 5.0 kJ/cm^2, used also for the 2-steps treatment for the fabrication of the 2D periodic texturing.

But diamond cathodes are not only based on the black diamond technology. Other innovative techniques are merged with a p-i-n structure designed within the project [7] (Fig. 11).

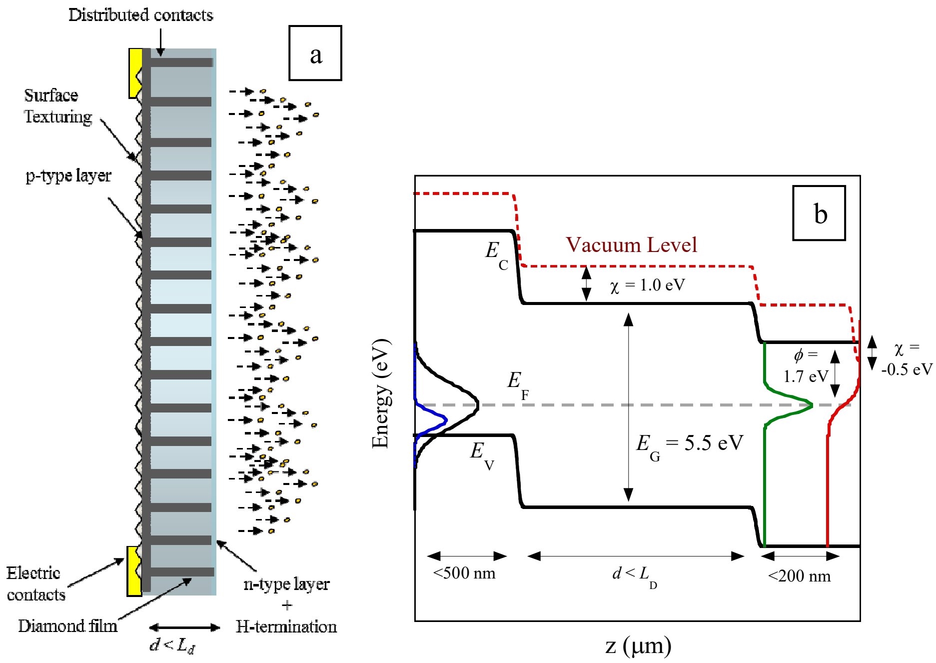


Fig. 11. a) Structure and b) band diagram of black diamond cathode.

The first one is the fabrication of embedded graphite distributed contacts within the diamond bulk, obtained by an ultrashort pulsed laser beam (coupled to a dedicated optics system) able to locally turn diamond into graphite in a controlled way [8]. The aim is the minimization of the electric resistivity of the embedded graphite microcolumns for refilling of the emitted electrons from the external circuit. Significant effort was dedicated to the optimization of microcolumns' physical properties, with the study (by using conductive AFM and Raman spectroscopy, see Fig. 12) of the individual and combined effect of laser pulse energy, translation velocity during the treatment, and number of treatment passes. Optimal parameters were used for fabricating the black diamond cathode with a 100 × 100 column array (Fig. 13), characterized by a resistance of 36.5 Ω at room temperature, slightly decreasing with increasing temperature (Fig. 14). Process yield (i.e. columns effectively conducting) was 83%, and the mean electric resistivity measured was 0.75 Ω cm, a value in line with the best resistivity values reported in literature, but with room for further improvement [9].

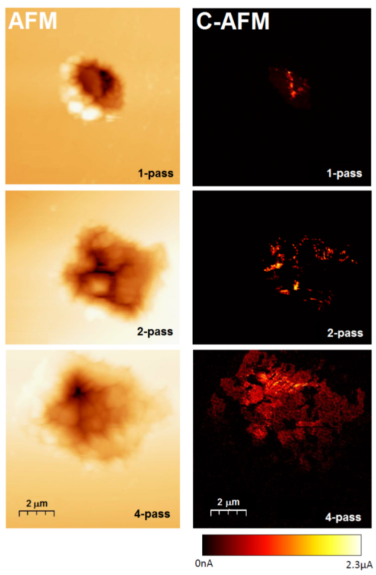


Fig. 12. AFM and conductive AFM allowed the correlation between morphology and electrical resistivity.

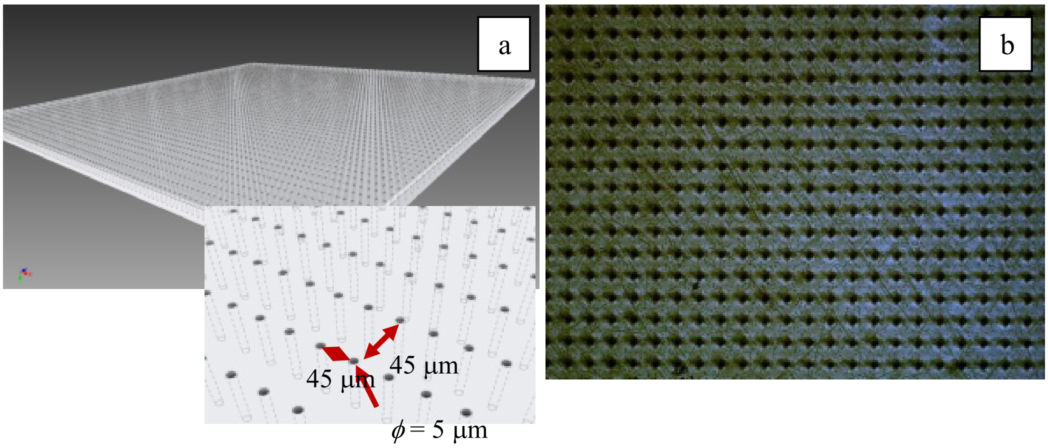


Fig. 13. Distributed graphitic electrodes composed by 10k microcolumns in the cathode. From a) design to b) fabrication.

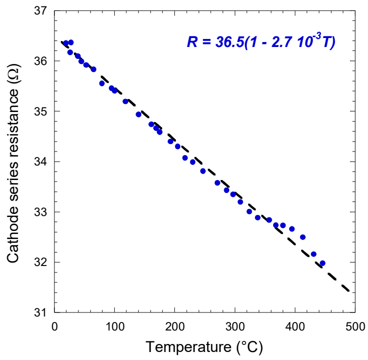


Fig. 14. Thermal dependence of cathode resistance after fabrication of the microcolumn array.

A p-type layer was fabricated by ion implantation of boron ions, followed by a thermal annealing at temperatures >1000 °C (Fig. 15), aimed at: 1) acting as a low-resistance layer towards electric contacts; 2) minimizing electron-hole recombination by the formation of a proper band-bending able to locally separate the charge carrier types; 3) increasing the photoelectric boost by introducing further useful energy states in the diamond bandgap, which add to the ones generated by surface nano-texturing [10]. The analysis of the influence on electrical and optical properties of the resulting films was carried out by varying the ion beam kinetic energy at a constant dose, and successively by varying the dose at the optimal kinetic energy. The best conditions were found for a treatment with an ion beam energy of 40 keV, whereas the influence of dose (from 10^{14} to 2×10^{15} ions/cm^2) needs still to be better clarified.

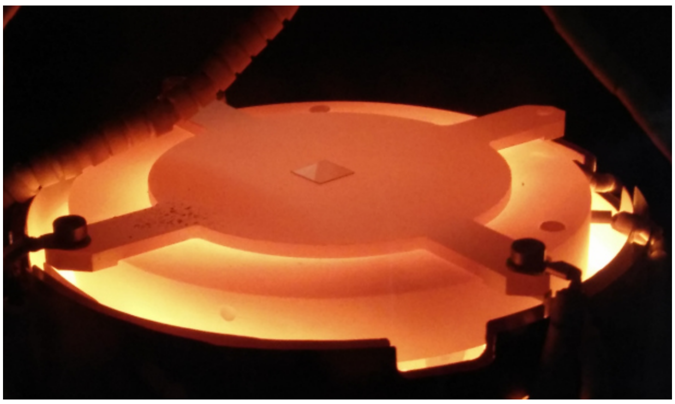


Fig. 15. Thermal annealing at 1100 °C of B-implanted diamond film.

A homoepitaxial deposition of n-type (nitrogen doped) diamond layer at the emitting surface was finally performed to obtain, in combination with a hydrogen termination [11], an effective work function estimated to be in the range 1.7 - 2.0 eV (Fig. 16).

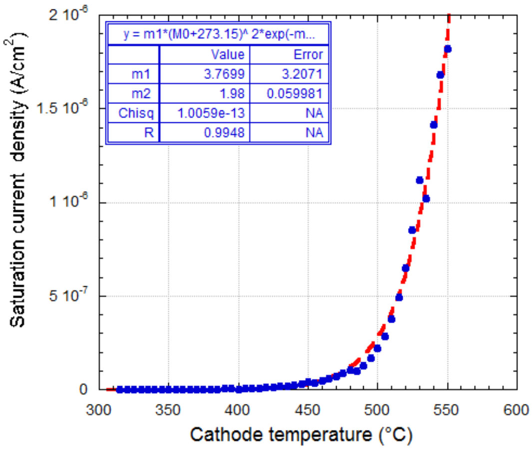


Fig. 16. Richardson-Dushman plot for the black diamond cathode after deposition of N-doped layer on the emitting side. The best fit is compatible with a work function of 1.85 ± 0.15 eV.

The recipe, consisting of the addition of nitrogen within the reaction gases, was optimized for single-crystal films. After the first attempts, resulting in the deposition of nanocrystalline films, the optimal recipe application induced a very low number of defects (mainly threading dislocations and hillocks) on the deposited layer, ensuring a good structural quality of the grown crystal (Fig. 17).

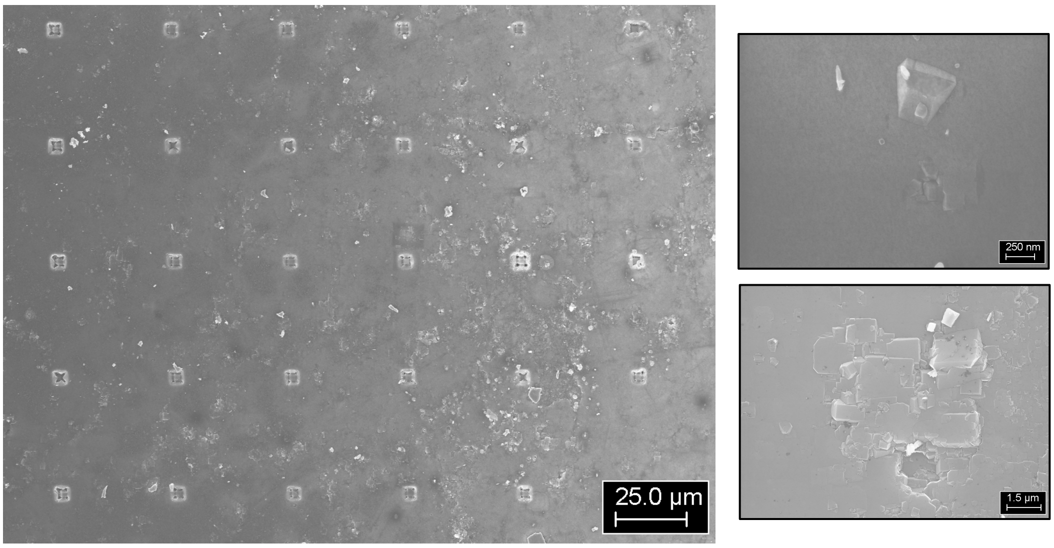


Fig. 17. Emitting surface after deposition of N-doped single-crystal layer. The microcolumn array is visible and diamond growth tends to fill the pit associated with the microcolumn fabrication. On the right, structural defects as threading dislocations and hillocks are visible.

The final black diamond cathode was metallized on the illuminated surface with a frame of sputtered molybdenum, followed by a thermal annealing under ultra-high-vacuum conditions.

c) Polycrystalline diamond membranes. Among the three proposed device structures, the *defect engineering strategy* applied at the nanoscale by Technion Institute resulted in the fabrication of diamond membranes acting as PETE cathodes (Fig. 18).

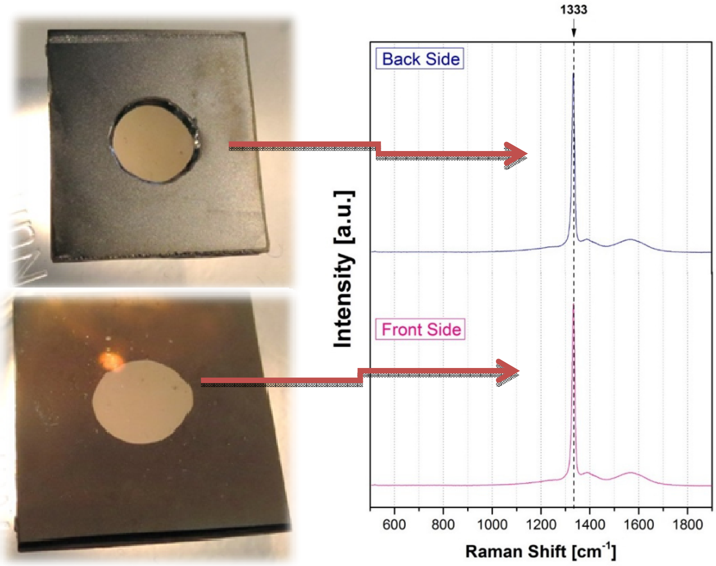


Fig. 18. Back and front side of a diamond membrane, with the associated Raman peaks demonstrating the good quality of the diamond crystal.

Small-grain polycrystalline diamond films are able to absorb visible radiation and, with a controlled defect density, also infrared radiation. Films have grain boundaries acting as distributed electric contacts for a reduction of the cathode series resistance (Fig. 19).

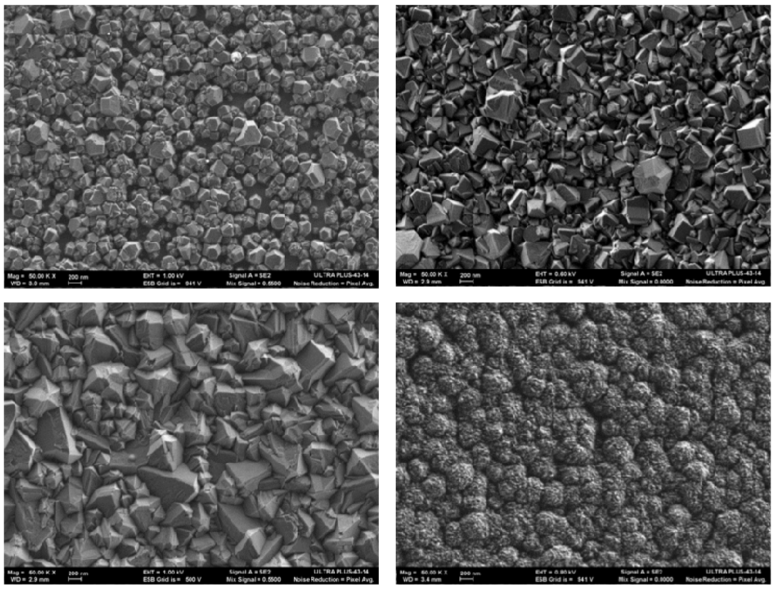


Fig. 19. Scanning electron micrographs of the surface of diamond films differing in the deposition parameters.

Silicon, used as a frame to mechanically support the diamond membrane, may also interact with the sunlight and inject charge carriers into the diamond films. In the framework of the project, Technion produced surface-hydrogenated diamond films of high quality supported by a silicon frame, and studied the behaviour and stability with temperature of the carbon-hydrogen bond [12-14] (Fig. 20).

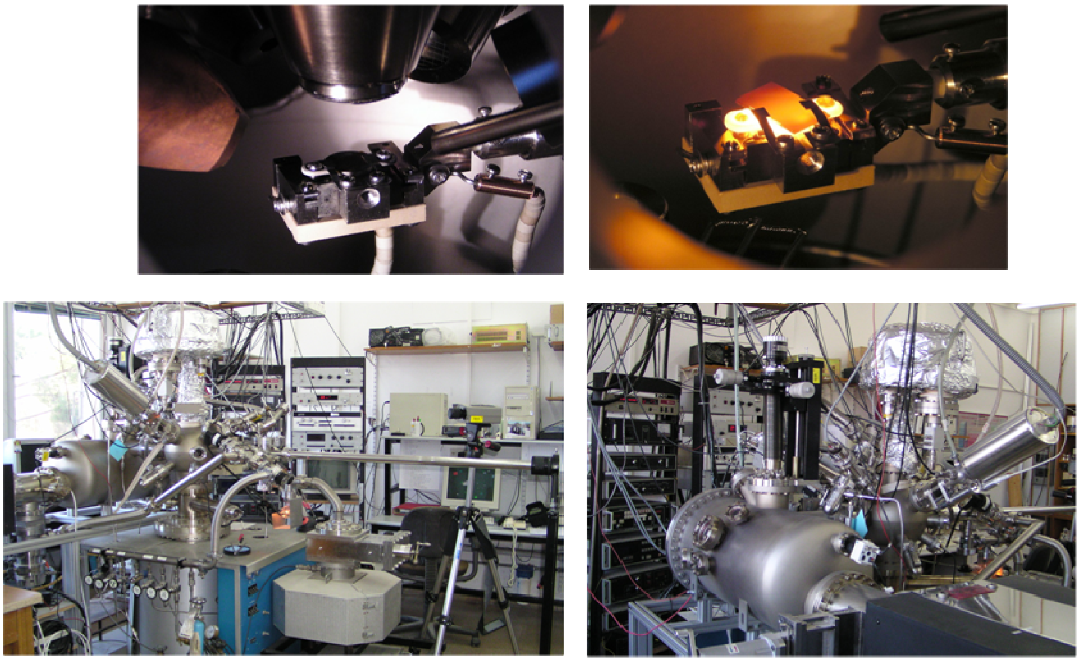


Fig. 20. Spectroscopy techniques in Technion for the chemical and physical surface characterization of diamond films.

Emitting surface was nitrogen-doped. Doping was obtained by adding ammonia in gas phase during film growth and/or after-growth nitridation by plasma or ion implantation [15-16]. PETE measurements performed with lasers (Fig. 21) allowed for the identification of a trap-assisted PETE mechanism based on the electronic contribution to the emission of shallow trap levels (0.04 – 0.16 eV from conduction band minimum).

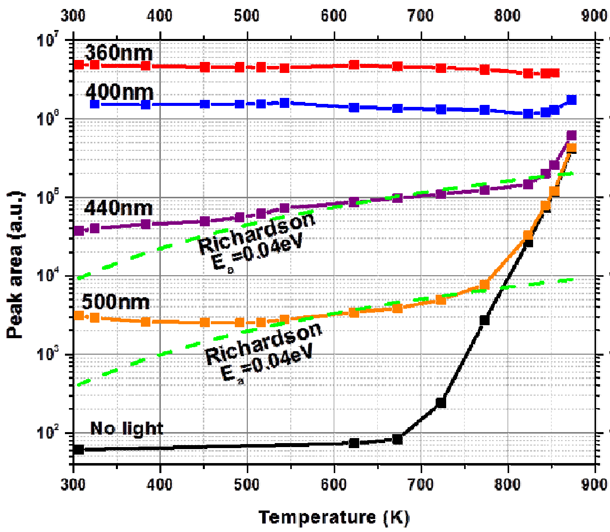


Fig. 21. Electron emission signal as a function of temperature at different illumination wavelengths. Trap-assisted PETE effects are visible down to 440 nm, after that the emission signal vs temperature becomes constant.

Tests under solar simulator, not performed in the framework of the project because of unexpected setbacks with the experimental setup, are included in the research activities that will be pursued in the near future by Technion Institute, in collaboration with the other partners involved.

3.2. Development of engineered anode.

In all the thermionic energy converters, the development of low work-function cathodes, able to considerably increase emitted currents, as well as the consequent development of even lower work-function anodes, are both challenging research activities. The work function of the anode must be indeed lower than that of the cathode for maximizing the electron flow and, therefore, the conversion efficiency.

Anode engineering has similar objectives and tools of that described for developing low work-function coatings as emitters for III-V semiconductors, with the only difference of the starting substrates.

Molybdenum was selected as the anode substrate material to reduce the device series resistance, with possibly a polished surface able to efficiently reflect the blackbody radiation emitted by the cathode and the visible radiation not absorbed by the cathode (Fig. 22).

Fig. 22. Single-crystal molybdenum anode substrate that successively hosted dielectric microspacers.

3.3. Development of dielectric microspacers

The development of a dielectric spacer able to maintain a gap between the electrodes of few micrometres is a primary condition for the efficiency of a vacuum diode like the PETE converter. The optimal gap value mainly depends on the cathode operating temperature, but gaps larger than few micrometres certainly induce severe conditions of space charge, causing a strong reduction of the emission current. Conversely, gaps narrower than the optimal one (i.e. < 1.5 µm) are not desirable since the anode receives the effect of the near-field radiative energy transfer from the hot cathode, resulting in excessive heating.

The proposed technological solution is a microstructured thermal and electrical insulating film deposited directly on the anode surface. Micromachining represents an advanced technology to guarantee a robust gap definition and to minimize the contact area between the electrodes, and consequently reduce the thermal flow. The microspacers (Fig. 23) are made of stoichiometric alumina, characterized by a very low thermal and electric conductivity. The potentiality of the recipe, developed by Ionvac Process Srl in collaboration with CNR, is connected with the low deposition temperature, which is slightly higher than room one: in this way, commercial photoresist can be used for a patterned deposition based on the lift-off technique. Microspacers of 5 µm diameter × 1.5 µm height and pitch of 200 µm were successfully fabricated.

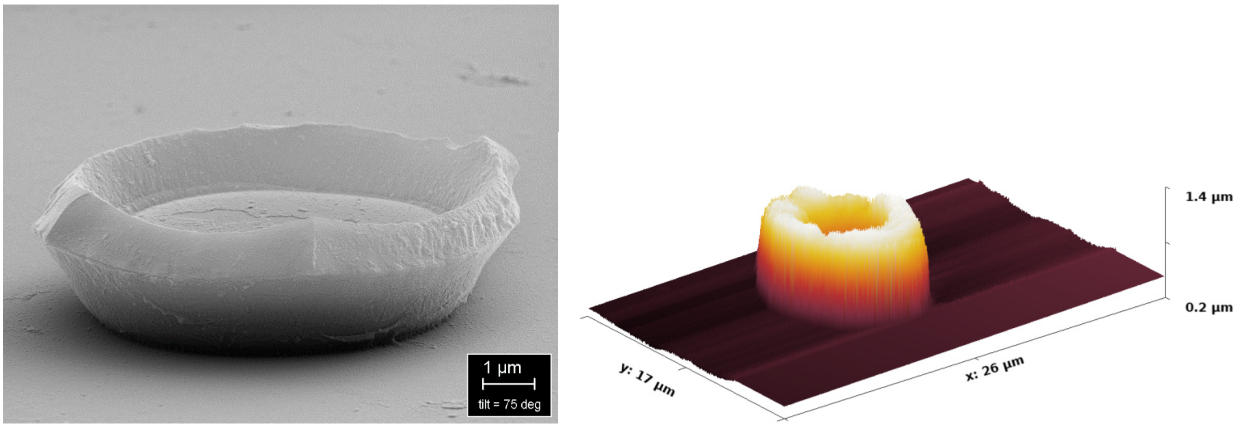


Fig. 23. a) Scanning electron and b) AFM micrographs of a dielectric microspacer.

A thermal simulation activity carried out by CNR demonstrated that a uniform distribution of microspacers on the anode is not desirable, since a temperature gradient is established from the centre to the anode periphery. Following this indication, microspacers were homogeneously distributed in the peripheral part of the anode, and disposed as radial lines passing for the centre, forming 45° sectors (Fig. 24).

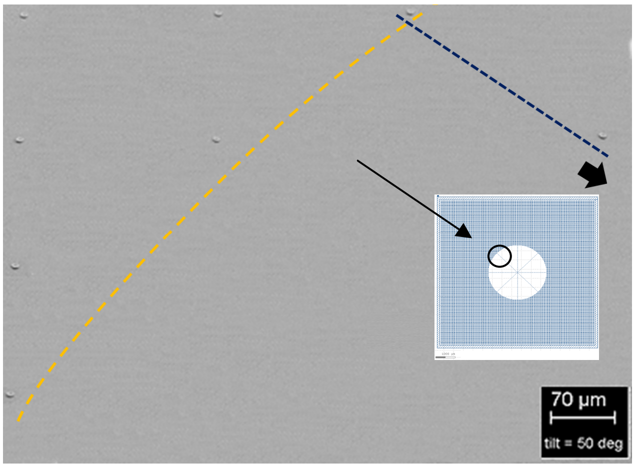


Fig. 24. a) Scanning electron and b) AFM micrographs of a dielectric microspacer.

3.4. Simulation models.

The development of simulation models guides experimental activities and, at the same time, receives feedback from them for a full validation of the methods. Starting from a 0D model representing an ideal cathode, Tel Aviv University made evolve it firstly into a 1D model, able to take into account layers with different physical properties. Finally, the model became 2D during the project activities, able to take into account contacts and shading effects for a refined prediction of the cathode performance (Fig. 25).

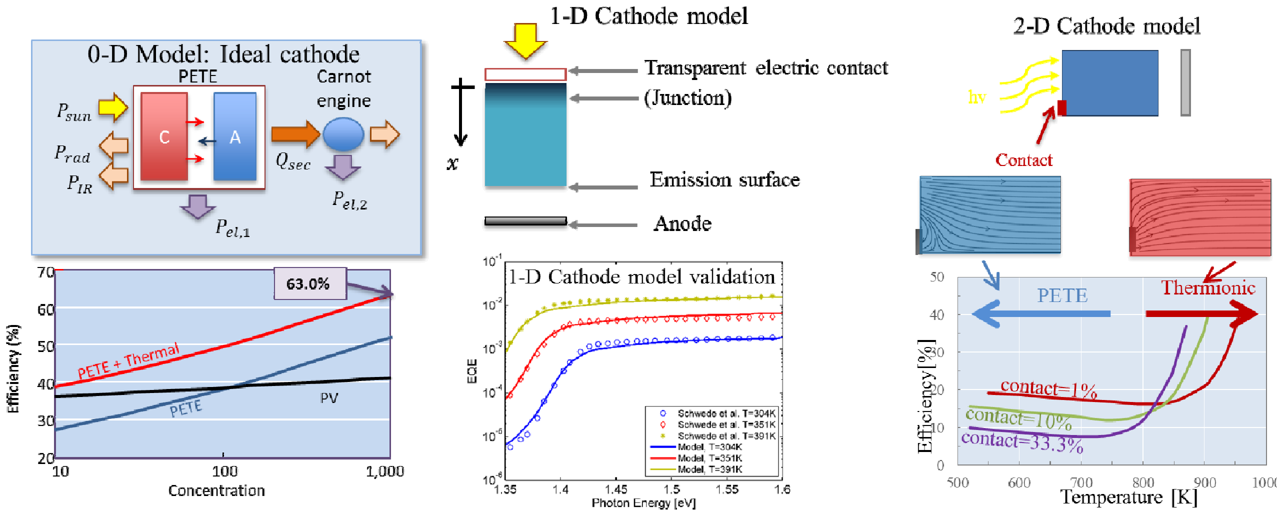


Fig. 25. Sketch showing the evolution from a 0D model to the 2D model.

The inter-electrode space effect was modelled with the 1D model finding that, for a fixed operating temperature, the efficiency decreases with flux concentration, due to the increased negative space charge losses [17]. However, when a thermal balance is applied, an optimal flux concentration is defined for every inter-electrode spacing width. In order to operate efficiently under a flux concentration of 1000 suns, the gap between the electrodes must be below 2 μm (Fig. 26).

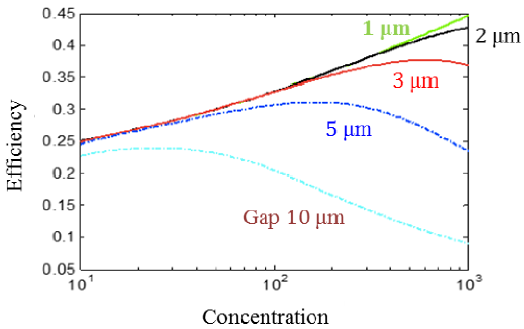


Fig. 26. Dependence of efficiency on concentration ratio at different inter-electrode gap values.

The model was able also to determine the limit for the parasitic series resistance in the anode and electrical leads, that must be below 0.1mΩ for flux concentration of 1000 suns (Fig. 27).

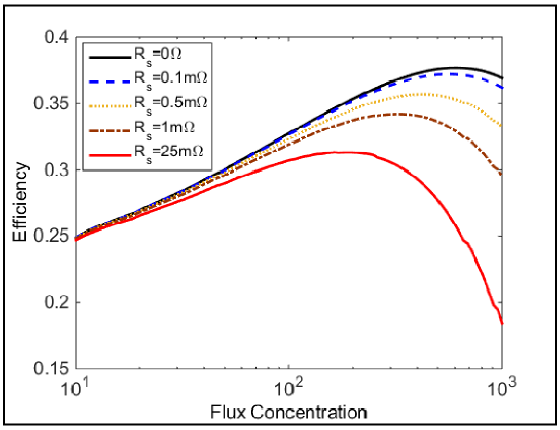


Fig. 27. Dependence of efficiency on concentration ratio at different parasitic electric resistance.

Operations of III-V phosphide-based cathode were simulated in detail [18], by deriving a quasi-realistic conversion efficiency. The 1D model applied to the 3rd generation structures allowed for the calculation of the conversion efficiency for given values of electron affinity, with and without considering space charge effects (Fig. 28). A maximum efficiency close to 13.5% was evaluated even at low flux concentrations (<50 suns).

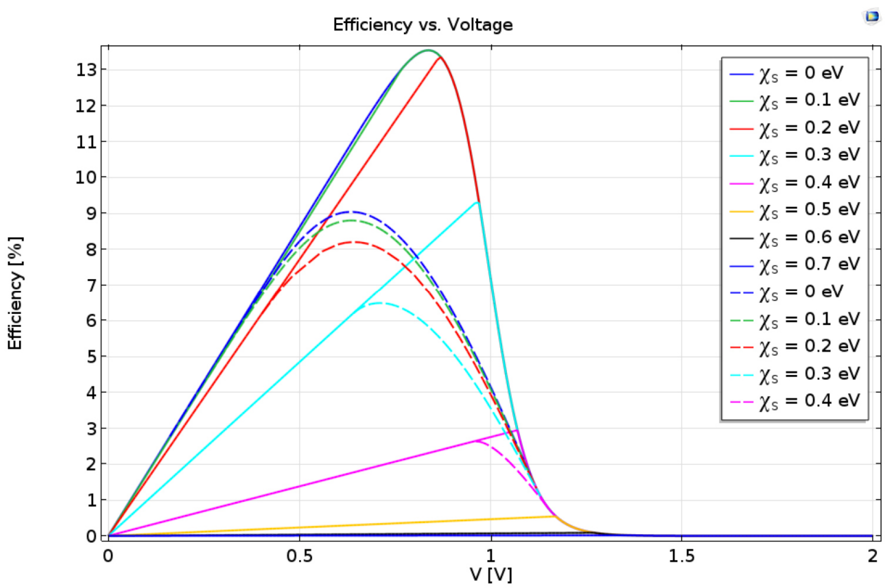


Fig. 28. Dependence of efficiency of third generation III-V cathodes as a function of retarding voltage. Solid lines are obtained without considering space charge effects, dashed lines by considering them.

By means of the 2D simulation model, additional mechanisms were studied as the effect of the position of electric contacts with respect to the flow of electrons and holes (Fig. 29). This analysis induced optimizations of the converter like the shifting of the contacts to the emitting surface for obtaining a lower inner resistance, thus driving the evolution from the 1st phosphide cathode generation up to the 3rd one. Conversely, the 3D complexity of the black diamond cathode and the spatial anisotropy of the diamond films composing the membranes hampered the possibility of simulating their operating behaviour during the project activities.

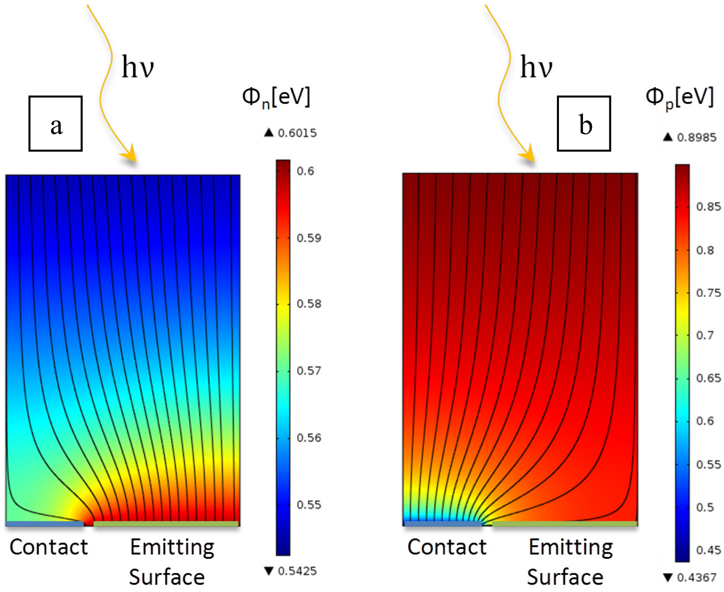


Fig. 29. Streamlines showing the trajectories of (a) electrons and (b) holes. The colour scale shows the quasi-Fermi energy for electrons and holes.

Finally, a system composed by a number *n* of single PETE conversion modules was modelled and simulated by Exergy Ltd (Fig. 30). All the PETE anodes were connected to a single heat pipe feeding an Organic Rankine Cycle (i.e. secondary conversion stage), the fluid of which was selected among the commercial available ones to improve overall conversion efficiency. The system operating behaviour was simulated by varying input radiation flux and anode temperature.

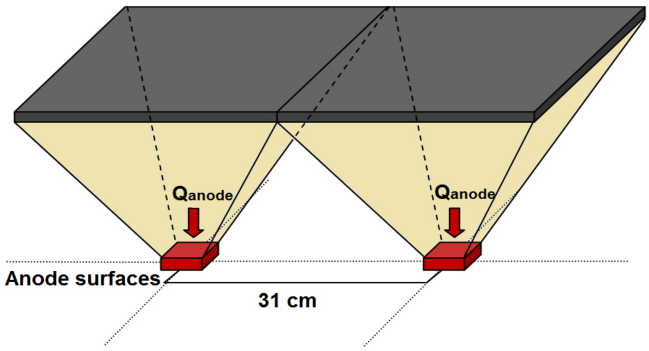


Fig. 30. Schematic of two conceptual PETE modules.

3.5. Knowledge of the physical properties of semiconductors and related structures at high temperature.

Many characterization techniques were used to quantify at high temperature the physical properties involved in the development of all the technologies. This is a secondary project output; however it represents, together with a large number of scientific papers (several of them open access readable), a cultural heritage for the semiconductor community, and includes also data for defect-engineered and wide bandgap semiconductors, usually more distant from the use of standard characterization techniques. A large part of these data is still being analysed and rationalized for its integration within future scientific papers.

3.6. Testing of the structures under realistic conditions.

a) Dedicated experimental setup. The developed technologies were tested for the first time under a high-flux solar simulator, in conditions close to the operating ones. A dedicated experimental tool was developed by Ionvac Process in collaboration with CNR and assembled at Tel Aviv University. This represents by itself an advanced technological result.

Equipped with easily dismountable anode and cathode holders, it was designed to reach ultra-high-vacuum conditions (Fig. 31). The electrode planarity can be adjusted by three actuators mounted at 120° and the distance between the electrodes can be adjusted by a micrometre-resolved linear translator, coupled to calibrated metal tips for obtaining a rough initial position. Laterally, closed by a vacuum gate, a source was mounted to thermally evaporate *in-situ* Cs dispensers on the anode and a filament to crack hydrogen molecules, able to restore an ideal hydrogenated surface on diamond. An IR window made of ZnSe was mounted laterally to the PETE components for calibrated thermal measurements with pyrometer and thermal camera. The system can be considered as very close to a commercial product for future qualification of PETE components.

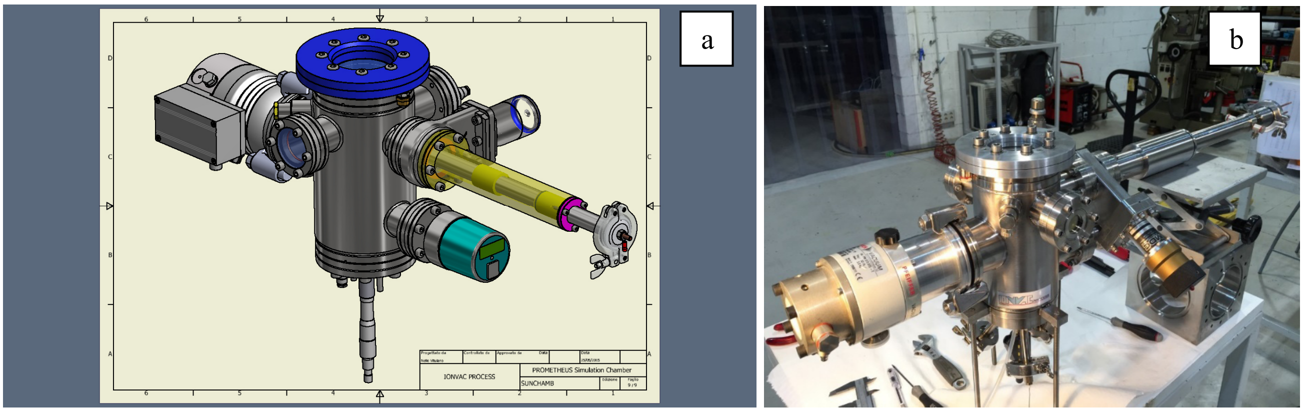


Fig. 31. Experimental setup from a) design to b) fabrication.

b) Experiments.

The setup was assembled in front of a high-flux solar simulator, equipped with a mirror for visible radiation, a hydrogen gas inlet, a cooling system with controllable coolant flow-rate and temperature sensors for deriving thermal balance on the anode. A cooled shutter with a discrete number of positions was mounted to modulate the radiation intensity (Fig. 32). The radiation power was measured with spatial resolution before the beginning of the experiments, and found to achieve a maximum value of 15.1 W (at 100% intensity) over the 6 mm diameter hole for cathode illumination. The corresponding radiation flux has an average value of 53.5 W/cm^2 (i.e. about 535 suns).

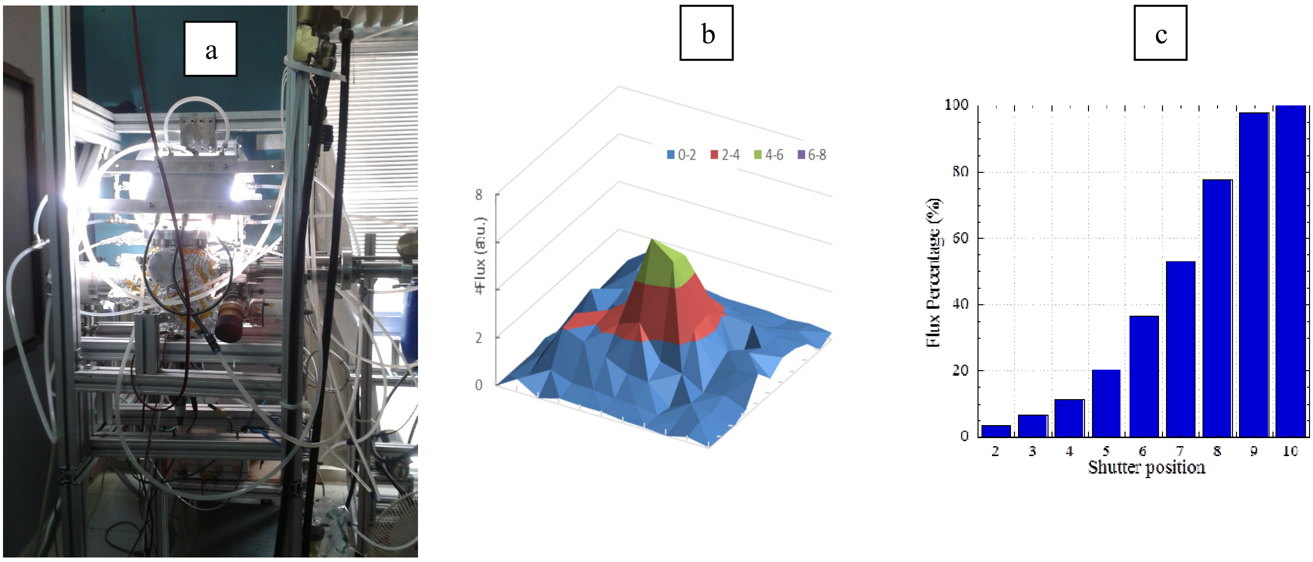


Fig. 32. a) Testing setup assembled with high-flux solar simulator; b) map of flux distribution; c) percentage of maximum radiation power modulated by the adjustable shutter position.

Black diamond and GaInP cathodes were tested up to 750 and 450 °C (Fig. 33), respectively. Black diamond cathodes demonstrated to be a promising technology for PETE conversion, whereas GaInP cathodes still suffer from a non-optimized emitting layer or from the presence of oxides on the surface. Diamond membranes, unfortunately, could not be characterized in time for presenting significant results by the end of the project.

Experimental results are still under revision, but already highlight that some improvements have to be introduced in a short time in the experimental procedure. Furthermore, the consortium prefers now to maintain the results reserved for the European Union and not to make them public. Obviously, it is intention and interest of the consortium to release them in a short time to the scientific, industrial, and civil communities.

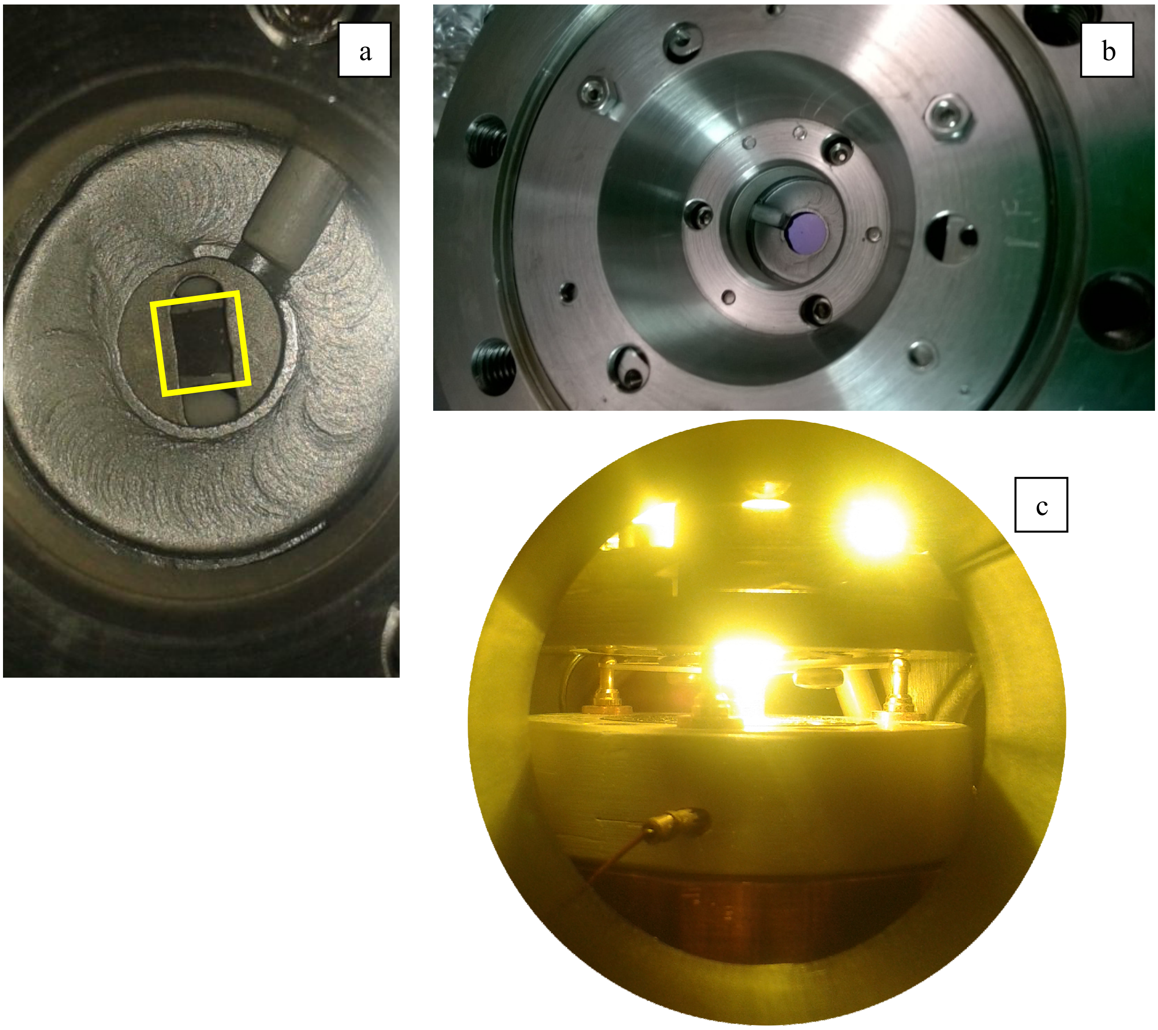


Fig. 33. a) Black diamond and b) GaInP cathodes mounted before the final testing. c) Picture taken from a lateral viewport during the experiments.

4. References from the project results

[1] G. Segev, Y. Rosenwaks , A. Kribus, “Limit of efficiency for photon-enhanced thermionic emission vs. photovoltaic and thermal conversion”, Solar Energy Materials and Solar Cells 140 (2015) 464-476.

[2] P. Calvani, A. Bellucci, M. Girolami, S. Orlando, V. Valentini, A. Lettino, and D. M. Trucchi, "Optical properties of femtosecond laser treated diamond", Applied Physics A, 117 (2014) 25-29.

[3] P. Calvani, A. Bellucci, M. Girolami, S. Orlando, V. Valentini, R. Polini, A. Mezzetti, F. Di Fonzo, and D. M. Trucchi, "Infrared absorption of fs-laser textured CVD diamond", Applied Physics A, 122 (2016) 3, 211.

[4] P. Calvani, A. Bellucci, M. Girolami, S. Orlando, V. Valentini, R. Polini, and D. M. Trucchi, "Absorptance enhancement in fs-laser-treated CVD diamond", Physica Status Solidi A 212 (2015) 11, 2463-2467.

[5] P. Calvani, A. Bellucci, M. Girolami, S. Orlando, V. Valentini, R. Polini, and D. M. Trucchi, “Black Diamond for Solar Energy Conversion”, Carbon 105 (2016) 401-407.

[6] A. Bellucci, P. Calvani, M. Girolami, S. Orlando, R. Polini, and D. M. Trucchi, “Optimization of Black Diamond Films for Solar Energy Conversion”, Applied Surface Science 380 (2016) 8-11.

[7] A. Bellucci, P. Calvani, M. Girolami, and D.M. Trucchi, “Defect Engineering of Diamond Cathodes for High Temperature Solar Cells”, 2015 IEEE Proceedings, (2015) 1616-1619 – ISBN: 978-1-4799-7992-9.

[8] M. Girolami, A. Bellucci , P. Calvani, S. Orlando , V. Valentini , D.M. Trucchi "Raman investigation of femtosecond laser-induced graphitic columns in single-crystal diamond", Applied Physics A, 117 (2014) 143-147.

[9] M. Girolami, L. Criante, F. Di Fonzo, S. Lo Turco, A. Mezzetti, A. Notargiacomo, M. Pea, A. Bellucci, P. Calvani, V. Valentini and D. M. Trucchi, “Graphite distributed electrodes for diamond-based photon-enhanced thermionic emission solar cells”, submitted to Carbon (2016).

[10] A. Bellucci, P. Calvani, M. Girolami, V. Carcelen, S. Michaelson, A. Hoffman, and D. M. Trucchi, “Buried Boron-Doped Layer for CVD Diamond Photo-Thermionic Cathodes”, IEEE Transactions on Nanotechnology 99 (2016).

[11] S. Iacobucci, Paola Alippi, P. Calvani, M. Girolami, F. Offi, L. Petaccia, and D. M. Trucchi, “Electronic structure of hydrogenated diamond: Microscopical insight into surface conductivity”, Physical Review B (2016) accepted for publication

[12] Sh. Michaelson , M. Chandran , S. Zalkind , N. Shamir , R. Akhvlediani , A. Hoffman, “Dissociative adsorption of molecular deuterium and thermal stability onto hydrogenated, bare and ion beam damaged poly- and single crystalline diamond surfaces”, Surface Science 642 (2015) 16-21.

[13] S. Elfimchev , Sh. Michaelson, R. Akhvlediani, M. Chandran, H. Kaslasi, A. Hoffman"The impact of surface hydrogenation on the thermionic electron emission from polycrystalline diamond films", Physica Status Solidi A, 211 (2014) 10, 2238-2243.

[14] Sh. Michaelson, T. Berkovitz, R. Akhvlediani, A. Hoffman, "Dissociative adsorption of molecular deuterium on polycrystalline diamond films activated by medium surface temperature", Physica Status Solidi A, 211 (2014) 10, 2313-2318.

[15] M. Chandran , M. Shasha , Sh. Michaelson , A. Hoffman, “Nitrogen termination of single crystal (100) diamond surface by radio frequency N2 plasma process: An in-situ x-ray photoemission spectroscopy and secondary electron emission studies”, Applied Physics Letters 107 (2015) 111602.

[16] M. Chandran , M. Shasha ,Sh. Michaelson , R. Akhvlediani , A. Hoffman "Incorporation of nitrogen into polycrystalline diamond surfaces by RF plasma nitridation process at different temperatures: Bonding configuration and thermal stabilty studies by in situ XPS and HREELS", Physica Status Solidi A, 212 (2015) 11, 2487-2495.

[17] G. Segev , D. Weisman , Y. Rosenwaks , A. Kribus, “Negative space charge effects in photon-enhanced thermionic emission solar converters”, Applied Physics Letters 107 (2015) 013908.

[18] A. Kribus, G. Segev, "Solar energy conversion with photon-enhanced thermionic emission", Journal of Optics, 18 (2016) 7.

5. The potential impact

The successful completion of several $ProME^3ThE^2US^2$ objectives paves the way to future products in the field of renewable energy science: high-temperature solar-cells for concentrated solar energy conversion. In particular, the impact can be specified provisionally in:

Short-term impact. Some technological approaches could achieve the validation of their feasibility at a lab level (TRL 4) like: 1) surface textured polycrystalline diamond films, which could be used in a very near future as selective absorbers for photo-thermal applications; 2) wafer bonding, which can be extended to other semiconductor devices.

Moreover, the hardware developed can be put directly on the market with minimal improvements: magnetron sputtering for stoichiometric alumina, magnetron sputtering for large-area alkali metal deposition, and PETE testing setup.

Finally, in the shortest terms, the project already has locally influenced the job employment with 19 researchers, 5 technicians, and 6 PhD students specifically recruited for its activities. About the 60% of them will remain working with the related employer.

Medium-term impact. $ProME^3ThE^2US^2$ results present potential medium-term benefits for the European economy and society, the most important of which is that it is "green", being non-toxic for human health, being a non-critical raw material (differently from other semiconductors used in solar cells), and contributing to a more efficient use of solar radiation. A well-known key element of the EU policy is indeed the target to reduce greenhouse gas emissions by 80%–95% of the 1990 levels by 2050. The system proposed in the project can act in the future as a topping cycle of Concentrated Solar Power (CSP) systems, and therefore perfectly falls within such purview: CSP is considered for the next future one of the most cost-effective technologies for reduction of CO_2 emissions. In the International Energy Agency (IEA) roadmap, CSP is expected to produce 2200 TWh/year from 630 GW of installed capacities by 2050: CSP could provide 11.3% of global electricity.

1. Economy. $ProME^3ThE^2US^2$ is expected to propose a high-impact system in terms of conversion efficiency and cost-effectiveness, as required by CSP industry. Efficiency values >40% would make the technology superior to multi-junction PV cells (with a nominal efficiency of 45% but an actual one ≈ 25%). Moreover, CSP energy production is expected to increase by 10% with a 20% decreasing technology cost, leading to a generation cost savings up to 50% by 2025. An added-value of $ProME^3ThE^2US^2$ technology is the compatibility with additional conversion stages or with energy storage systems, useful to overcome the limitations of intermittent power sources and satisfy the daily energy demand.
2. European competitiveness. EASAC (European Academies Science Advisory Council) examined the current status and development challenges of CSP, considered as a real alternative to fossil fuels, and evaluated the potential contribution of CSP in Europe and in the MENA (Middle-East Northern-Africa) region until 2050. EASAC states that the solar resource in the Mediterranean region is such that CSP could provide a significant contribution to achieve the European aim of a zero-CO_2 electricity system by 2050. An internal production located in Southern Europe and an import of CSP-generated electricity from MENA region could strongly reduce dependence on fossil fuels. A solar technology with advantages in scalability, high-efficiency, compatibility with energy storage, non-toxicity could be the key-factor for boosting EU competitiveness.
3. Society. Local benefits brought by CSP are significantly higher than for other renewable technologies such as PV. CSP fosters economic development by creating local jobs, wealth and expertise. Europe encourages the establishment of strong international partnerships, particularly

with neighbouring Countries, by promoting actions to integrate energy markets and regulatory frameworks, and to launch a major cooperation with Northern Africa on energy initiatives. In such a context, ProME^{3}ThE^{2}US^2 consortium was assembled to have a Mediterranean contribution (Italy, Spain, France, Israel), in order also to promote and exploit the development of an enhanced CSP technology directly in the EU-MENA Countries, where CSP could have a large social impact.

It's worth mentioning here that a *frontier technology* successfully tackled in ProME^{3}ThE^{2}US^2 is the development of dielectric microspacers for establishing a few micrometres gap between the electrodes. If the future ageing tests will be successful, potentially it may represent a revolutionary technology for every thermionic energy conversion in the medium term, thus enabling to surpass huge limitations caused by space charge effects. It is noteworthy considering that space charge effects historically induced the development of technological complications in thermionic devices like vapour addition within the active volume or the use of magnetic fields.

Long-term impact. The long-term impact of this intrinsically scalable solid-state technology may range from small concentrating systems to solar tower fields, and be applied to domestic, industrial, and rural decentralised contexts. ProME^{3}ThE^{2}US^2 technology with some rearrangements can be exploited also for aerospace applications (e.g. propulsion in inner solar system) and industrial heat recovery: the estimated potential savings via industrial waste-heat recovery from thermal sources has been estimated to be from 2% to 14% of final energy consumption.

Another long-term impact will be the further application and the extension of the defect engineering scientific concept, that produced a completely novel material – the black diamond – to other wide bandgap semiconductors, with the possibility of inspiring a huge range of applications up to now precluded to them. Indeed, the black diamond technology opens the route to an *original engineering and scientific strategy applied to semiconductor materials*. The concept of *intermediate band semiconductor*, namely the introduction of a defect band within the bandgap, only obtained up to now by the development of technologically very complex nanostructures (e.g. quantum dots), was radically redefined within the project, which proposed several frontier processing methods for the implementation of an intermediate band in a bulk semiconductor (e.g. definition of periodic defects on the surface, sub-surface, and even bulk crystal lattice). However, a precise control of such techniques still has to be optimized: with this aim, the understanding of the effects of size, periodicity, form, and depth of the defected structures on the electronic and optical properties has to be tackled by a significant additional simulation and modelling activity.

6. Contact details & website

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