

Photovoltaics: A leadership to regain

A great effort from Europe is needed in order to regain market share and rebuild the credit of its companies. Italy and, in particular, ENEA is ready for this challenge pointing to the evolution of c-Si solar cell, new thin film absorber and new PV components

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Photovoltaics (PV) is the most popular source of renewable energy today. It offers an important option to address the environmental issue of reducing CO₂ emissions, but it is still heavily demonized because of the high cost and the need for incentives for its full market penetration. However the relative figures worldwide tell us of a healthy market with two-digit annual growth, even if in some countries, mainly in Europe, it is suffering a reduction because of reconsiderations of government support policies. In Italy –which is the leading country for PV contribution to the national electric demand (8.2%)– the end of incentives has led many to declare the death of PV which however, after suffering from

the initial shock, is re-stabilizing at more reasonable values, far from the past years insane growth (370 MW installed in 2016; 600 MW annual installation expected in 2020). World market data and projections, even in conservative scenarios, seem to agree about the possibility of reaching the installation threshold of 100 GW/year by 2020, taking advantage of new technology options. A quick overview of the PV status worldwide indicates that global installations, in the year 2016, have exceeded the cumulative power of 300 GW (305 GW).

PV market: The Asian kingdom

The annual installations reached the value of 75 GW, scoring yet a growth

of 50% compared to 50 GW of 2015. China leads the ranking of annual installations with 45.6% of the global market, thanks to its 34.2 GW of installed capacity in 2016, followed by USA with 13 GW and then by Japan, that has added 8.6 GW in the year. To notice the 5 GW installed in India, an increase of 150% compared to 2015. Europe, already in sharp decline in the previous years, sees its market share (8.6% in 2016) to lose about 5 points, despite a moderate decline of total installations of 0.5 GW compared to 2015 (total European installation in 2016 hits 6.5 GW). To be pointed out the installations in the United Kingdom with 1.9 GW, followed by Germany (1.2 GW), nowadays very far from the 7.5 GW recorded in 2010-2012.



A closer look to the market indicates that about 70% of module production is localized in China and Taiwan while only 5% is in Europe and 3% in USA and Canada. The cell and module production is dominated by crystalline silicon (c-Si) with standard or advanced processes with a share of 94% of annual production, leaving the remaining 6% to thin film technologies. So it is not surprising that the ranking of the top 10 world producers shows 3 Asian companies in the top 3 positions and 8 Asian companies in the full list. It is interesting to observe that the huge supremacy of Asian firms was built on a tremendous growth of production capacity based on standard c-Si solar cell technology (c-Si p-type Multi, Al-BSF), with costs reduction realized by scale economy. Only recently companies are starting a transition to advanced c-Si cell processes like PERC, HJT and Rear Junction solar cell. Without modifications, this evolution will allow the persistence of the Asian supremacy for the years to come, with a marginal role of European companies in the PV scenario. The concerns of Euro-

pean stakeholders resulted into the activation of different bodies for the goal of regaining a “Global Leadership in Photovoltaics”. This target is the current strategy of the European Strategic Energy Technology Plan (SET-Plan) aiming to synergize the actions of bodies like EU PV Tech Platform (PVTP), EU Construction Tech Platform (ECTP), EERA Joint Programme on PV (EERA-JP-PV), EU Platform of Universities in Energy Research & Education (EUA-EPUE). It is a coordinated action with ambitious and clear objectives for Europe, among which:

- Growth of research and innovation investments.
- Challenging PV system cost and performances targets (+20% by 2020 and +35% by 2030 module efficiency; -20% by 2020 and -50% by 2030 system cost compared to 2015 values).
- Strong synergy with key sector of building industry.

The latter objective is driven by the innovations needed for the Zero-Energy Buildings and Plus Energy

Buildings (PEB) which require new materials and concepts and innovative combination of Building Integrated Photovoltaic (BIPV) with energy efficient building materials. The building is going to be the elemental component of the future smart grid in which PV generation, energy efficiency, storage and management can transform a current niche market into an huge business opportunity for European companies. Italy will contribute to this effort working on almost all the components of the PV value chain, thanks to the high wealth of knowledge and technological skills in its research centers and universities. In particular, ENEA –the Italian public research body having the highest commitment in PV for human resources and investment– is working on new technological options embracing both the evolution of c-Si solar cell and new thin-film absorber as well as BIPV with new vision of photovoltaics in the living environment. In what follows, a more detailed description on ENEA activities is given.

Towards high efficiency solar cells

Solar cells based on silicon achieve a high sunlight conversion efficiency due to the material quality and widespread technological know-how. Silicon is abundant raw material with low toxicity and its technologies are scalable for mass production, as demonstrated by the photovoltaic market share of silicon-based cell higher than 90%. Improving the efficiency of Si solar cells is key to further reduce the energy cost and the surface of photovoltaic field, thus leading photovoltaics to the 20% share of the global primary energy demands by the year 2050 [1]. Amorphous/crystalline heterojunc-

tion (a-Si:H/c-Si HJ) cell has recently demonstrated to be the most effective way to achieve the theoretical efficiency limit of 29.1% on c-Si based solar cell [2]. Indeed, the HJ cell efficiently merges the advantages of widespread technological know-how on c-Si material and capability of thin amorphous films to produce, with a low thermal budget, high surface passivation with recombination velocity below 10 cm/s. Indeed the great amount of hydrogen content within the amorphous film, useful to passivate network dangling bonds, at the same time represents a reservoir of hydrogen available to passivate, under certain conditions, the c-Si surface on which the amorphous thin film is deposited by Plasma Enhanced Chemical Vapor Deposition (PECVD) technique. To this aim, an intrinsic layer about 5-6 nm thick is used as a buffer before doped film to reduce defect density at the a-Si:H/c-Si interface. Emitter and base contacts of the cell are then performed by 10 nm of doped a-Si:H film. While very effective base contact can be obtained by n-type a-Si:H/i-a-Si:H/n-type c-Si due to optimal work function alignment at interface, tunneling mechanism is instead required to ensure the same performance of p-a-Si:H/i-a-Si:H/p-c-Si base contact. Poor lateral conductivity of doped a-Si:H films is overcome by Transparent Conductive Oxide film commonly deposited on top and bottom sides of the cell by sputtering process of Indium Tin Oxide film. Its thickness is chosen also to work as antireflection coating. The metal electrodes of the cell are commonly performed by expensive screen printed Ag grid as obtained by low temperature sintering Ag pastes. On the other side high c-Si material quality with a

minority carrier lifetime of 10 ms and prolonged durability have been recently demonstrated by n-type doped c-Si wafer leading to less than 0.5% per year total efficiency reduction under sunlight exposure for at least 35 years.

To enhance the cell efficiency and reduce the cell costs, several approaches can be suggested.

One of the most effective is moving both base and emitter contacts to the rear side of the cell, as suggested by the Interdigitated Back Contact cell that frees the cell front side from the shadow grid. Even this approach has been successfully demonstrated by homojunction c-Si based cell of Sun Power, the use HJ technology for both contacts allows higher Voc values with respect to the homojunction and a thermal budget lower than 250 °C that allows to use thinner wafers with respect to the conventional ones.

To further enhance the cell efficiency, thin film a-Si:H undesired absorption of the sunlight can be reduced by introducing wider energy band-gap a-SiOx for both surface passivation and emitter or base contacts. Recently, studies are demonstrating this new material is more stable to higher temperature steps useful to overcome the issue of cell interconnections within the module. Actually this is obtained by tape instead of soldering to avoid thermal stress at the interfaces, but the tape interconnections leads to lower module fill factor due to higher series resistance with respect to the conventional technology of module manufacturing. Furthermore, to reduce the cell cost and simplify the cell fabrication, the doped thin amorphous films, commonly formed by toxic PH₃ or B₂H₆ gasses, can be replaced by transparent not stoichiometric oxide

as MoO_x or NiO_x, WO₃ for p-type and SnO_x or TiO₂ for n-type contact. These promising materials can be obtained by conventional technologies as Sputtering, Thermal Evaporation or Spin Coating that can be easily scaled up to large industrial mass production at lower cost with respect to PECVD systems.

Finally the expensive silver grids electrodes will be soon replaced by copper plating, thus reducing the cell costs and enhance electrodes conductivity, indeed the screen printed silver grid has a conductivity one order of magnitude lower than plated Cu.

Moreover, the HJ technology easily approaches cell and module bifaciality, indeed perfect passivation is obtained by thin film on both front and rear sides of the cell and both contacts are completed by transparent conductive oxide followed by silver grid electrodes, therefore the cell is always ready to be bifacial. Bifacial module can produce even more than 20% energy per year with respect to monofacial and this value can be further enhanced considering that the HJ thermal coefficient is lower than that of c-Si homojunction leading to a higher amount of energy under the same sunlight and thermal conditions.

All these suggestions are under investigation in ENEA Labs to enhance the cell efficiency above the current 18%. This road is the core of the Horizon 2020 Ampere project, led by Italian PV company, aiming to get modules with 23% efficiency at 0.45 €/Wp using a bifacial configuration. Future efficiency enhancement will be achieved by tandem cell design in which two cells will be stacked in series. To this aim the top cell is devoted to the UV/visible part of the sunlight spectrum and the bottom

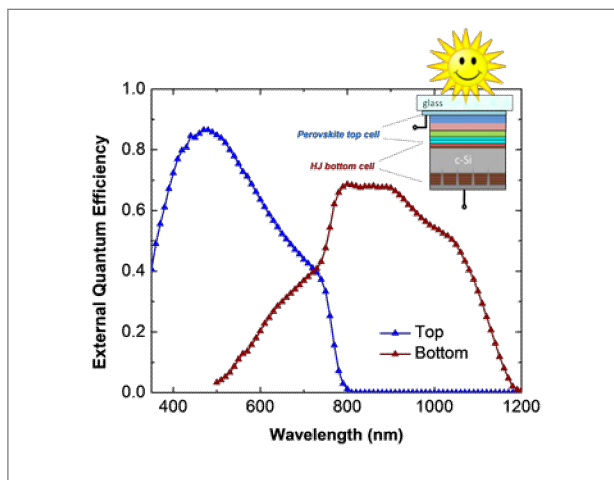


Fig. 1 Quantum efficiency of a tandem cell

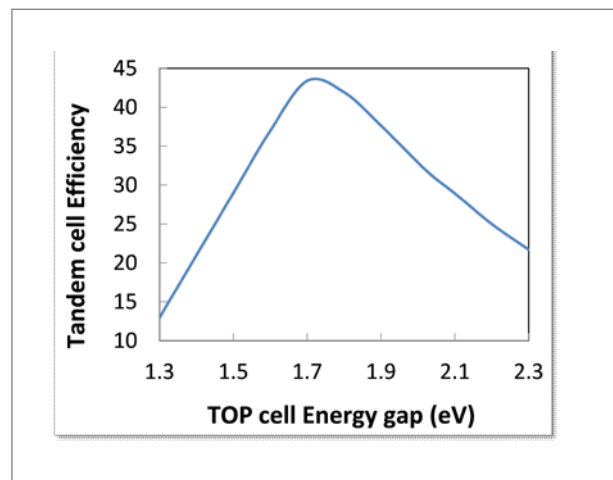


Fig. 2 Tandem cell efficiency as a function of top cell energy bandgap with c-Si bottom cell

cell is specialized to Near-IR light collection, as shown by the quantum efficiency of a tandem cell born from a collaboration between ENEA and CHOSE (Centre for Hybrid and Organic Solar Energy - University of Rome Tor Vergata) and reported in Figure 1.

Both cells have to be tuned, in terms of absorption and thicknesses, to achieve at least half of the total photocurrent of a single c-Si based cell, while the total cell voltage must be higher than the double of a single c-Si cell. Following this approach, solar cell efficiency as high as 40% can be theoretically demonstrated rightly choosing the energy bandgap of the absorber material in the top cell while the bottom cell is c-Si based, as shown in Figure 2 [3].

Perovskite and kesterite for the top cell of a tandem device

Aiming at the described high efficiency tandem cell, the challenge is the synthesis of absorber material for top cell which is flexible in tuning to the desired bandgap for the best matching with c-Si bottom

cell. Several class of materials have been proposed such as chalcogenide semiconductors, organic-inorganic perovskite, and III-V semiconductors (such as GaInP). The research in ENEA is focused on the development of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) and hybrid organic-inorganic perovskite solar cells because of the potential advantages of these absorber materials in term of costs and availability of the constituent elements with respect to other possible options. These activities are mainly supported by the Italian Ministry of Economic Development in the framework of the Operating Agreement with ENEA for the Electric System Research and are carried out in cooperation with several Italian Universities.

Earth-abundant CZTS photovoltaic devices

All successfully commercialised non-concentrating photovoltaic technologies to date are based on silicon or on chalcogenide thin-films (semiconductors containing Group VI elements, specifically Te, Se, and S). The success of this last

option can be ascribed to the high device performance reached with this class of materials: the record efficiency of CdTe is 22.1%, while $\text{Cu}(\text{In,Ga})(\text{Se,S})_2$ (CIGS) presents a record value of 22.6%, making it the highest-efficiency thin-film solar cell material to date [4]. Unfortunately Cd and Se are toxic “heavy metals”, while Te and In are among the 12 most scarce elements in the Earth’s crust, factors that would seem to clearly limit the long-term potential of the established chalcogenide technologies. However the compound $\text{Cu}_2\text{ZnSnS}_4$ is similar to CIGS involving earth-abundant, non-toxic elements (the scarce element In is replaced by Zn and Ga replaced by Sn). CZTS can crystallize to form either a kesterite or stannite crystal structure, with kesterite being preferable for PV applications. Despite the relatively small effort so far devoted to the development of this material, initial results have been promising with a group at IBM reporting 12.6% efficiency for small cells, obtained replacing part of sulphide with selenide (CZTSS), while an efficiency of 9.5% has been obtained with CZTS

absorber by University of New South Wales (Australia) [4].

The CZTS bandgap is 1.5 eV, a value very close to the optimal bandgap for a single junction solar cell of 1.35 eV. Moreover, alloying with related compounds to replace, for example, Sn by Si will increase the bandgap making values more suitable for the top cell in a two-cell stack on silicon. Polycrystalline films of CZTS are made using sputtering or evaporation from the constituent elements and are typically deposited onto a Mo film that is sputtered on a soda-lime glass substrate. The typical active layer thickness is ~ 1 to $3 \mu\text{m}$. The cell is finalized by the chemical-bath deposition of CdS to form a heterojunction followed by an intrinsic ZnO buffer layer and a transparent ZnO:Al conducting layer.

The main research activities in ENEA are focused on: 1) improving the control and the reproducibility of the CZTS growth process (the CZTS films are prepared by sulfuration of precursors, co-sputtered from SnS, ZnS, and Cu targets); 2) evaluating the effect of the disorder in the distribution of Cu and Zn cations, which gives rise to band gap fluctuations that reduce carrier mobility and increase recombination; 3) evaluating buffer layers alternative to CdS, such as for example Zn_2SnO_4 , in order to improve the device performance and avoid the use of toxic Cd. At present, the best CZTS solar cell developed in ENEA presents an efficiency of 7.8%.

Perovskite solar cells

Hybrid organic-inorganic perovskite solar cells have recently taken the PV research world by storm, with efficiencies above 20% achieved after only 5 years of substantial work: the

present record efficiency of 22.1% has been obtained by the Korea Research Institute of Chemical Technology (KRICT) [4]. Perovskite-based solar cells are generally fabricated with organic-inorganic trihalide perovskites with the general formula ABX_3 , where A is the methylammonium (CH_3NH_3) (MA) or formamidinium [$\text{HC}(\text{NH}_2)_2$] (FA) cation, B is commonly lead (Pb), and X is a halide (Cl, Br, or I). Depending on the halide used, the band gap can be continuously tuned from ~ 1.5 eV (pure I) to 3.2 eV (pure Cl), with the smaller-band gap materials providing better solar cell efficiencies. Mixed-cation perovskite solar cells have consistently outperformed their single-cation counterparts: The first perovskite device to exceed 20% of efficiency was fabricated with a mixture of MA and FA [5]. Recent reports have shown promising results with the introduction of caesium mixtures, enabling high efficiencies with improved photo-, moisture and thermal stability [6].

The perovskite salts form polycrystalline films with a perovskite structure at or near room temperature by precipitation from a variety of polar solvents (commonly dimethyl formamide or dimethyl sulfoxide). The typical device is realized on FTO-coated glass substrate coated with an electron selective contact (usually TiO_2). Subsequently, the perovskite is deposited using various methodologies such as sequential deposition, solvent engineering, vapor-assisted deposition, vacuum evaporation, etc. Finally, the hole-selective top contact (usually Spiro-OMeTAD) is spin-coated on top, and the back contact (usually gold) is evaporated to finish the device.

Despite their excellent initial performance, hybrid perovskite solar

cells are known to degrade under standard operating conditions; at present this is the greatest barrier to commercial implementation. The origins of perovskite cell instability are currently a topic of active research, although photoreduction by ultraviolet light and reactions with water have already been identified as likely candidates. Also, measurements of the current-voltage characteristics can suffer from hysteresis, making efficiency analysis complex. Because of Pb toxicity, encapsulation and recycling are important for this technology to become viable for large-scale application.

ENEA is currently developing perovskite solar cells under ambient conditions, studying the effect of the relative humidity on the device performance. The best efficiency of 12% has been measured on cells prepared at a relative humidity of about 40%. The devices have been realized in collaboration with CHOSE that, in particular, has optimized the electron selective contact in TiO_2 . ENEA is also studying the possibility to improve the properties of the electron selective contact using materials and processes compatible with the tandem architecture by developing ZnO nanorods grown on sputtered AZO (Figure 3). Preliminary tests on devices have shown very promising results. Furthermore, ENEA and CHOSE are involved in the development of a single-junction perovskite solar cell with a transferable architecture for monolithic tandem solar cells on silicon. Preliminary prototypes of perovskite/Silicon tandem devices have been already realized with efficiencies of about 16%, by mechanically connecting the two component cells (quantum efficiency shown in Figure 1).

Use of photovoltaics in the living environment

In the context of the possible uses of photovoltaics in the living environment, main focuses of research activity are architecture and landscape issues, as well as measurements, testing and standardization issues. The use of photovoltaics is investigated with regard to technological and design issues, and to cultural issues too (social acceptance of new technologies). Attention is also given to new methodological and theoretical frameworks for the implementation of photovoltaics in the living environment. Since 2000, research has been carried out about the use of photovoltaic technologies in buildings, and the main results are patents, innovative prototypes, and scientific publications and books.

Some of these prototypes are installed in the ENEA Research Centre in Portici (Naples), such as a coloured glass-glass photovoltaic façade and a street lamp (Stapelia™), which integrates photovoltaic cells and LEDs, and having an in-

novative design as its main feature. Moreover, in the same Research Centre since many years, the laboratory “Test over Photovoltaic Modules”, is also in operation, which has obtained the accreditation certificate no. 1421 by Accredia in January, 2014. Its activity is focused on module quality evaluation, reliability, and life time estimation.

More recently, the topics of the integration of photovoltaics with the landscape, and the use of photovoltaics in net-zero-energy and smart buildings, have been included in the research domain.

In this framework ENEA participates in several European research programmes and in a number of international networks. In particular, significant activities have been carried out under the International Energy Agency (IEA), on the following topics: Solar technologies and architecture; Solar energy and urban planning; Net Zero Energy Buildings design; Acceleration of BIPV. Among other activities, ENEA is a frontrunner on the design of photovoltaics as an element of the landscape. In this

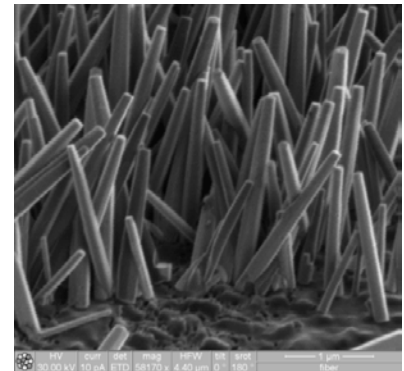


Fig. 3 SEM image of ZnO nanorods for perovskite solar cells

regard, since 2011 ENEA organizes a thematic event –Photovoltaics | Forms | Landscapes– on the occasion of the European Photovoltaic Solar Energy Conference (EUPVSEC), within the framework of a memorandum of understanding with the European Commission, JRC. Moreover, ENEA is actively involved in the COST action RELY, on Renewable Energies and Landscape Qualities.

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