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Polycrystalline Cu(InGa)Se₂/CdS Thin Film Solar Cells Made by New Precursors

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1. Introduction

In the last five years photovoltaic modules production continued to be one of the rapidly growing industrial sectors, with an increase well in excess of 40% per year. This growth is driven not only by the progress in materials and technology, but also by incentives to support the market in an increasing number of countries all over the world. Besides, the increase in the price of fossil fuels in 2008, highlighted the necessity to diversify provisioning for the sake of energy security and to emphasize the benefits of local renewable energy sources such as solar energy. The high growth was achieved by an increase in production capacity based on the technology of crystalline silicon, but in recent years, despite the already very high industrial growth rates, thin film photovoltaics has grown at an increasingly fast pace and its market share has increased from 6% in 2006 to over 12% in 2010. However, the majority of photovoltaic modules installed today are produced by the well-established technology of monocrystalline and polycrystalline silicon, which is very close to the technology used for the creation of electronic chips. The high temperatures involved, the necessity to work in ultra-high vacuum and the complex cutting and assembly of silicon "wafers", make the technology inherently complicated and expensive. In spite of everything, silicon is still dominating the photovoltaic market with 90% of sales. Other photovoltaic devices based on silicon are produced in the form of "thin films" or in silicon ribbons; these devices are still in the experimental stage. Amorphous silicon is a technology that has been on the market for decades and it is by now clear that it does not keep the promises of change and development that were pledged when it was initially launched.

Without resorting to sophisticated photovoltaic devices such as multi-junction solar cells, where the cost of production is high, thin film silicon modules were generally poor in conversion efficiency and demonstrated low stability. On the other hand, silicon is not an appropriate material for implementation as a thin film, both for the difficulties of processing (necessity of high temperatures) and the inherent characteristics of the semiconductor which, being an "indirect gap" material has a low absorption coefficient in the visible radiation region. Because of this, silicon must either be deposited in thick layers or it is necessary to use complex light trapping techniques. Beyond the use of silicon, thin film technology has the advantage to provide large-scale productions, in which the panel is the final stage of in-line processes and not the assembly of smaller cells, as in the case of crystalline silicon or polysilicon wafer-based modules. The highest rates of production (in terms of square meters of modules per minute) have assumed since the '70s, that, in the future, in order to compete with traditional energy sources, there will be just thin film modules. However the effective start of industrial production of thin film modules was delayed until 2000 due to problems with the reproducibility of the results, the stability over time and scalability of the layer deposition on large areas. Overcoming these problems, the photovoltaic modules that use CuInGaSe₂ (CIGS) and CdTe thin film technology are already being produced with a high quality and conversion efficiency (12-14%), with expected values up to 15% for the near future. The cell interconnection integrated into large area modules (0.6 x 1.2 m²), with very limited use of raw materials, can minimize the production cost, so that the thin film modules will soon be able to compete with conventional modules based on the silicon wafer.

In addition to lowering the cost/m² of the cell area, thin film technology offers the possibility to produce devices on flexible substrates. This extends the opportunity to installing modules by adapting them to the shape of the surface thereby achieving complete architectural integration.

Moreover, Cu(InGa)Se₂ polycrystalline thin film modules have successfully passed the long-term tests in outdoor conditions, demonstrating a very good stability over time.

Beyond the potential benefits associated with terrestrial applications we must also consider that the Cu(InGa)Se₂ showed good resistance to ionizing radiation, much more if compared with crystalline silicon cells; furthermore, the cells can also be made on very light weight flexible substrates. For these reasons, this material is very promising for space applications. From this point of view, Cu(InGa)Se₂ is one of the most promising materials used in thin-film technology; not only for the reasons mentioned above, but perhaps more importantly, because it has reached very high efficiencies comparable to that obtained, up to now, with the best Silicon solar cells, at both cell and module level.

The highest Cu(InGa)Se₂ solar cell efficiency of 20,3% with 0,5 cm² total area was gained in 2010 by Jackson et al. [1] from Zentrum fuer Sonnenenergie of Wasserstoff-und-Forschung Baden-Wuerttemberg (ZSW), Germany. In addition, many companies have made modules with efficiencies above 12% up to the fantastic world record of 17,8 % obtained with 30x30cm² modules by the "Solar Frontier" research group from Showa Shell Sekiyu KK (Japan), which exceeds the previous record of 17,4% achieved by the Q-Cells subsidiary company, Solibro Gmb H.

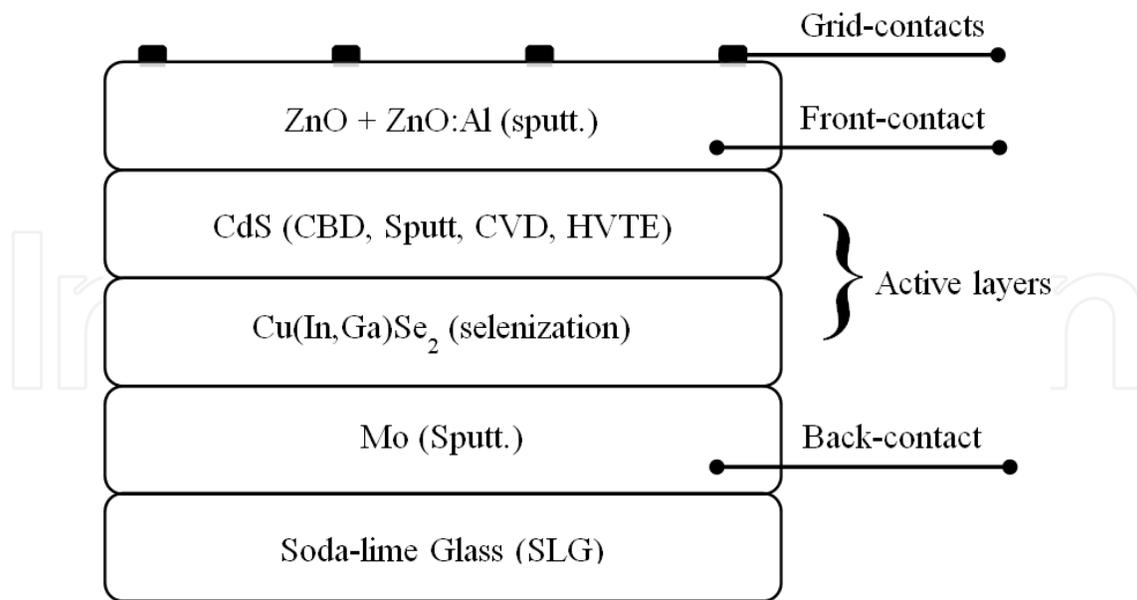


Figure 1. Schematic structure of a $\text{Cu}(\text{In,Ga})\text{Se}_2$ -based solar cell.

As we can see in figure 1, the $\text{CuInGaSe}_2/\text{CdS}$ thin film solar cell consists of 6 layers; this implies that in the overall structure there are at least 7 interfaces.

This made very complicated to understand the behavior of the final device and several research groups have tried to explain the properties of the cell by studying these interfaces in detail. On the other hand, when two different materials are put in contact there is an inter-diffusion of chemical elements from the one to the other and a subsequent formation of a new thin layer between the two. This new layer is known as *hetero-interface*. The most important hetero-interface is the metallurgical hetero-junction between $\text{Cu}(\text{InGa})\text{Se}_2$ and CdS , but all the other interfaces have also an important role in the final performance of the cell.

Despite all efforts aimed to understand the behavior of the interfaces, $\text{Cu}(\text{InGa})\text{Se}_2/\text{CdS}$ hetero-junction still exhibits quite a few open problems and it is therefore subject to a margin of uncertainty in its progress. For this reason more detailed studies are needed to reach a complete understanding of all the phenomena regarding this remarkable device.

In this chapter we will describe the current state and the degree of understanding of the $\text{Cu}(\text{InGa})\text{Se}_2$ solar cells construction technology. In particular, after presenting a brief history of this device we will discuss the material and consider both the cells and the modules; after that we will focus particularly on the manufacturing techniques which have led to high-efficiency devices (cells and modules) and consequently, the different problems inherent to this material with particular attention to the scalability at an industrial level of the production process. Then we arrive at conclusions also talking about future perspectives.

2. A brief history

The history of CuInSe_2 begins with the research carried out in the Bell Telephone laboratories in the early 70's. The synthesis and characterization have already been studied by Hahn in 1953 [2]. Along with new ternary chalcopyrite materials, it was also characterized by other groups [3]. The Bell Labs had grown crystals of a wide selection of these materials reporting their structural and electro-optics properties [4, 5]. In that period, a solar cell with an efficiency of 12% based on CdS evaporated onto a p -type CuInSe_2 single crystal was realized [6]. In 1977, depositing by flash-evaporation a CdS thin film onto a single crystal of p -type CuGaSe_2 , a solar cell that exhibited an energy conversion efficiency of up to 7 % was realized [7].

CuInSe_2 is a semiconducting compound of the I-III-VI₂ family with a direct band gap of 1,05 eV. Its chalcopyrite structure makes a good match to wurtzite CdS with only 1,2% lattice mismatch. This explains the good efficiency for the first time obtained with CuInSe_2 single crystal and put in evidence that $\text{CuInSe}_2/\text{CdS}$ was the sixth system, along with junctions based on Si, GaAs, CdTe, InP, and Cu_xS that showed energy conversion efficiency up to 10%. Besides, CuInSe_2 is a direct band gap semiconductor, which minimizes the requirements for minority carrier diffusion length, and exhibits the highest absorption coefficient ($3 \times 10^5 \text{ cm}^{-1}$) in the visible region of the solar spectrum. These considerations make CuInSe_2 the best-suited material for the fabrication of an all polycrystalline thin film solar cell.

There has been relatively little effort devoted to devices realized on a CuInSe_2 single crystal apart from this first work, because of the difficulty in growing high-quality crystals. But, the aforementioned properties of CuInSe_2 channeled all the attention to thin-film solar cells because of their intrinsic advantages. The first thin-film $\text{CuInSe}_2/\text{CdS}$ solar cell was fabricated by Kazmerski et al. in 1976 [8] by using films deposited by evaporation of CuInSe_2 powder in excess of Se vapor. This solar cell showed an efficiency of about 4-5%.

We had to wait until 1981 when, in the Boeing laboratories, the first high-efficiency all thin film solar cell based on the system $n\text{-ZnCdS}/p\text{-CuInSe}_2$ was realized with a conversion efficiency of about 9,4% and in 1985 they reached the efficiency of 11.4% [9].

Since the early 80's, ARCO Solar and Boeing have tackled the difficult issues involved with industrial production such as throughput and yield. These efforts have led to many advances in the technology of CuInSe_2 solar cells.

The two groups have characterized their R&D approaches in different ways. The diversity of the two approaches consists basically in the $\text{CuInSe}_2(\text{CISe})$ deposition methods, while the architecture of the device remains essentially the same.

The Boeing method includes the co-evaporation from separate sources of the single elements for CISe deposition. These films were deposited on alkali-free glass or ceramic covered by a thin layer of Mo, which acts as a positive electrode. The devices were finally completed by evaporating, on top of the CISe film, two layers of CdS (or ZnCdS), the first one was an intrinsic layer and the second one heavily doped with indium in order to ensure a best photo current collection.

The two methods, introduced by Boeing and ARCO Solar, still remain the most common techniques for producing high efficiency cells and modules. Boeing was focused on co-evaporation of individual elements from separate crucibles while ARCO Solar was more confident in a two-stage process in which a low-temperature deposition of Cu and In was followed by a heat treatment at high temperature in H₂Se ambient.

With the “Boeing” basic structure, in 1996 [10] was reached the fantastic result for an all thin film solar cell: a conversion efficiency of 17,7%! This improvement was obtained by using CuGa_xIn_{1-x}Se₂ as absorber layer. Effects of partial substitution of Ga for In appeared to be optimized for X=0,25. The band gap of the quaternary compound varies from 1,04 eV for X=0 to 1,7 eV for X=1; this means that the substitution of Ga for In causes an increase in open-circuit voltage, but a decrease in short-circuit current and fill factor and only for X=0,25 does the system reach the right equilibrium. Adjusting the Ga concentration profile into the absorber layer, in order to enhance the collection of the photo-generated carriers, it was possible to fabricate thin film solar cells based on the CdS/CuGaInSe₂ system with an efficiency of 18,8% in 1999 [11], of 19,2% in 2003 [12] and of 20.3% in 2011 [1]. This last result is the highest value for energy conversion efficiency in an all thin film photovoltaic device.

cell	Energy conversion efficiency %	reference
n-CdS/p-CuInSe ₂ single crystal (1974)	12	[6]
n-CdS/p-CuGaSe ₂ single crystal (1977)	7	[7]
n-ZnCdS/p-CuInSe ₂ all thin film (1976)	4-5	[8]
n-ZnCdS/p-CuInSe ₂ all thin film (1985)	11.9	[9]
n-CdS/p-CuInGaSe ₂ all thin film (1996)	17.7	[10]
n-CdS/p-CuInGaSe ₂ all thin film (1999)	18.8	[11]
n-CdS/p-CuInGaSe ₂ all thin film (2003)	19.2	[12]
n-CdS/p-CuInGaSe ₂ all thin film (2011)	20.3	[1]

Table 1. Representative CuInSe₂ and CuGaSe₂ based solar cells.

Let's summarize the key enhancements to the method that gave the more efficient cells (co-evaporation-Boeing).

1. Soda lime glass replaced ceramic or borosilicate glass substrates. This change was made for the lower costs of soda lime glass and its good thermal expansion match with CuInSe₂. An increase in processes tolerance and device functioning were the result. It was soon clear that the better results obtained came primarily from the beneficial inter-diffusion of sodium from the glass [13].
2. The high thickness of the In-doped CdS or ZnCdS film was replaced by a thin un-doped CdS layer followed by a conducting Al-doped ZnO (ZAO) film. This was effective in

increasing the photocurrent having enlarged the spectral response in the blue region wavelengths [14].

3. The absorber energy gap was increased from 1.02 eV for CuInSe_2 to 1.1–1.2 eV for Cu(In,Ga)Se_2 by the partial substitution of In with Ga, leading to an important increase in efficiency [15].
4. Innovative absorber deposition processes were developed to obtain energy gap gradients improving the photovoltage and current collection [16, 17].

Several companies around the world are coming to the market with Cu(In,Ga)Se_2 -based modules. The more advanced features are briefly shown in Table 2, where one can distinguish the two processes described above. One is the typical co-evaporation method of Shell Solar Industries, formerly Arco Solar and then Siemens Solar in California, Würth Solar and Solibro in Germany and Matsushita in Japan, with which these companies have announced modules efficiencies of around 12-13%. The selenization of metallic precursors in H_2Se ambients instead the technology used by Showa Shell that has announced module efficiency in excess of 14%.

Producers			Prodn. capacity MW/Year (since)	Glass-size (m x m)	Efficiency % max./med.	On the market
CIGS						
Bosch Solar	CISTech	(Johanna Solar, Ger.)	30 (2008)	0.5 x 1.2	--/9.4	No
Wuerth Solar, Ger.			14.8 (2007)	0.6 x 1.2	<13/11.7	Yes
Global Solar, USA			4.2 (2006)	1" wide metal sheet	10/8	Yes
ISET, USA			Pilot plant	0.6 x 1.2	10	Yes
MiaSolè, USA			150 (2012)	0.66 x 1.61	13	Yes
Showa Shell, Japan			20 (2007)	0.6 x 1.2	14.2/11.8	Yes
Honda Soltec, Japan			27 (2007/2008)	0.8 x 1.3	13/10	Yes
Sulfur Cell, Ger.			5 (2007/2008)	0.65 x 1.25	8.2/7	Yes
AVANCIS, Ger.			20 (from 2008)	0.65 x 1.6	13.1/12.2	Yes
Hanergy China (Solibro, Ger.)			25-30 (2009)	0.65 x 1.2	12	Yes

Table 2. Some manufacturers of CuInGaSe_2 thin-film photovoltaic modules, and their current market condition.

In addition a Phoenix Solar Holdings Corp subsidiary company, EPV Solar Corp, formerly Energy Photovoltaics, Inc. is using its own in-line evaporation process, International Solar Electric Technology (ISET) is developing a particle-based precursor for selenization, while Global Solar Energy (GSE) and MiaSolè are pursuing a process for roll-to-roll co-evaporation onto a flexible substrate with final efficiencies of around 15.5%.

Despite these encouraging results and the efforts made to develop the manufacturing processes, there remains a large difference in efficiency between the laboratory-scale solar cells and mini-modules, and the best modules on the market. In part, this is due to the need to develop innovative equipment for large-area, high-throughput deposition required for manufacturing thin-film photovoltaic's. Presumably, this is because the material has only been studied for use in photovoltaic applications, and many of the advances in scientific understanding of materials and technologies have been purely empirical.

However, in recent years, many enhancements in the scientific knowledge of the materials and device have been made and this has also led to evident improvements in manufacturing technology.

3. The history of CuInSe₂ and Cu(In,Ga)se₂ at the ThiFiLab

The Thin Film Laboratory (ThiFiLab) of the Physics Department at the University of Parma-Italy, started to work on CuInSe₂ in 1986 with the aim of achieving high quality films suitable to realize an all thin film solar cell made entirely using only the sputtering technique [18-22]. The first approach was the sputtering deposition of CuInSe₂ starting directly from stoichiometric targets. At this stage, great care was placed on the preparation of the substrates. As substrates 1 inch square Corning glasses 7059 were used. Glasses were covered with a 4 μm thick layer of Al deposited by sputtering at a substrate temperature of 350°C. The Al layer obtained was crystalline with an average grain size of 100 μm and with the (111) plane uniquely oriented along the glass surface. Since Al is not a good ohmic contact for *p*-type CuInSe₂, the Al film was covered with either a 0.2 μm thick layer of Mo or a 0.5 μm layer of Au; both these films were deposited by sputtering. Au was deposited on Al at a substrate temperature higher than 500°C. In this way, Au reacts with Al forming the metallic compound AuAl₂. This compound exhibits the cubic structure with a lattice constant of about 6 Å which is closer, in respect to any other metal, (Mo has a lattice constant of 3.15 Å) to the lattice constant of CuInSe₂ (5.78 Å). Both Mo and AuAl₂ thin films, prepared as previously described, were used as substrates for the sputtering deposition of CuInSe₂.

The RF magnetron sputtering system was provided with three targets like Mo, CuInSe₂ and CdS and a rotatable heating-etching station whose temperature could be controlled up to 600°C. Mo and CdS targets were supplied by commercial suppliers while the CuInSe₂ target was prepared in the ThiFiLabby synthesis in a high pressure furnace. In this case the liquid encapsulation technique was used, with B₂O₃ acting as the encapsulant. The crucibles had a flat bottom whose diameter was equal to that of the target holder in the sputtering system. In order to avoid the reaction between In and Se at a temperature lower than the B₂O₃ melting point (450°C) a pre-reacted Cu-In alloy instead of the individual elements was used. The reaction of components and melting were carried out under a 50 atm N₂ pressure. Several CuInSe₂ targets with different Cu/In ratios and one with an excess of Se with respect to the metals have been investigated. The substrate temperature was varied between 300 and

550°C. It was found out that stoichiometry, crystallinity, carrier type and resistivity of CuInSe_2 films depended on several deposition parameters, like the Ar pressure, R.F. power, bias applied to the substrate, substrate temperature and type of substrate, whether glass, Mo or AuAl_2 (see figures 2-3).

Among these, the substrate temperature and the bias applied to the substrate seemed to be the most effective. Stoichiometric films with good crystallinity were generally grown at a substrate temperature of around 450°C, with the substrate bias kept at a minimum value (self-biased substrate). $\text{CuInSe}_2/\text{CdS}$ solar cells were fabricated as depicted in figure 4.

Mo, CuInSe_2 and undoped CdS films were deposited in sequence in the same sputtering chamber without interrupting the vacuum [23, 24]. Mo and CuInSe_2 films were deposited at the same substrate temperature, between 400 and 500°C. In some cases, CuInSe_2 films were deposited on AuAl_2 covered substrates. The undoped CdS film was deposited at 200°C substrate temperature with an H_2 partial pressure in the sputtering chamber of about 1.5×10^{-4} mbar, that corresponds to 3% of the $\text{Ar} + \text{H}_2$ total pressure. These films exhibited resistivity in the range of $10^{-1} - 1 \Omega\text{cm}$ and were highly transparent in the wavelength region between 1.6 μm and the absorption edge of CdS (0.52 μm).

After that, a mechanical scribing was done in order to obtain an active cell area of about 0.2 cm^2 . The photovoltaic efficiency of such a cell was in the range of 5-8%. To achieve high efficiency cells it was necessary to use two CuInSe_2 layers, the first one Cu-rich and the second In-rich [25-27]. The low efficiency obtained with this technique was essentially due to the segregation of binary phases, like Cu_2Se in the first layer.

In order to overcome the segregation of binary phases some alternative techniques were studied; among them the selenization of stacked elemental layers seemed to be one of the most effective since the technique is very promising for large-scale application.

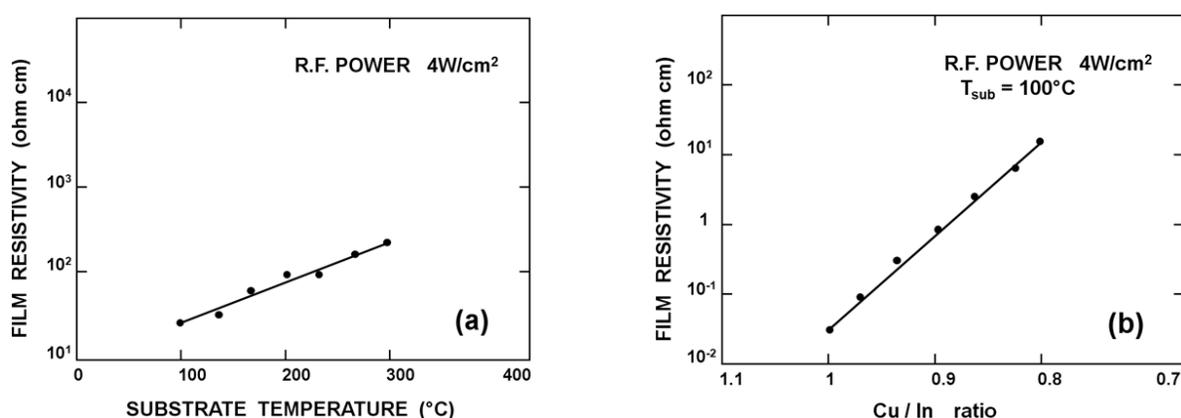


Figure 2. a) Resistivity of p -type CuInSe_2 films as a function of the substrate temperature. The Cu/In ratio in the target was 0.8 and no bias was applied to the substrate. (b) Resistivity of p -type CuInSe_2 films as a function of the Cu/In ratio in the target. The substrate temperature is 100°C and no bias was applied to the substrate. Redrawn from "Proceedings of the 18th IEEE Photovoltaic Specialists Conf., 1985, Las Vegas, Nevada, October 21-25. p. 1388-1392".

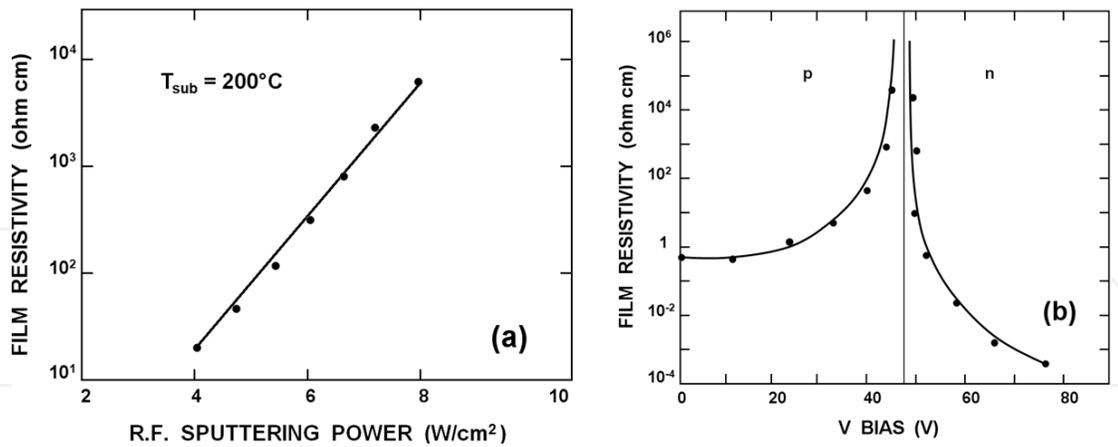


Figure 3. a) Resistivity of *p*-type CuInSe₂ films as a function of sputtering power. The Cu/In ratio in the target was 0.8 and the substrate temperature was 200°C. No bias was applied to the substrate. (b) Resistivity of both *p*- and *n*-type CuInSe₂ films as a function of the negative bias applied to the substrate. The Cu/In ratio in the target was 1 and the substrate temperature was kept at 250°C. Redrawn from "Proceedings of the 18th IEEE Photovoltaic Specialists Conf., 1985, Las Vegas, Nevada, October 21-25. p. 1388-1392".

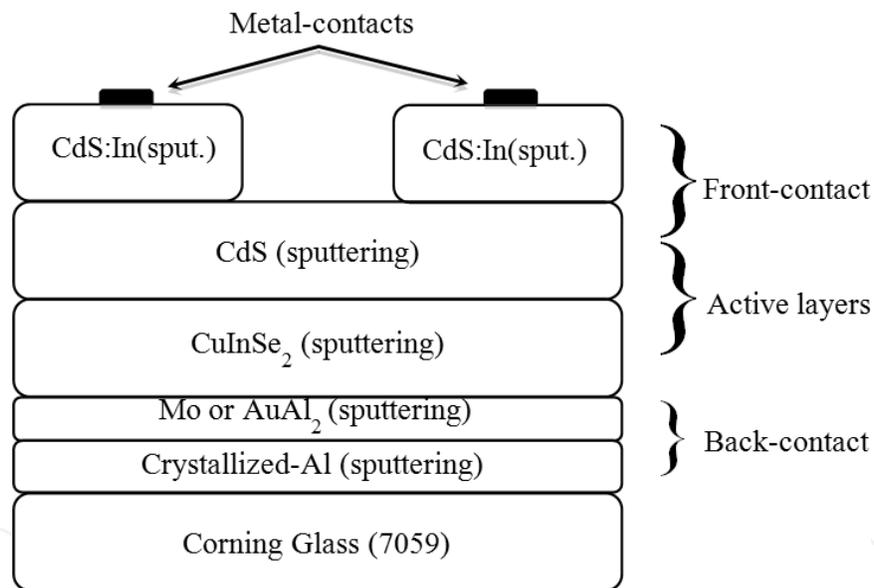


Figure 4. Structure of the all-sputtered thin film CuInSe₂ solar cell.

By using the same substrates described above, a 2500 Å thick Cu film and a 5600 Å thick In film were deposited by sputtering on top of the Mo layer. The deposition of Cu and In elemental layers was done at several temperatures, ranging from 50 to 220°C. After the deposition of the elemental layers, the sample was set inside an evaporation chamber for the selenization. The Se-vapor was obtained from a graphite boat kept 5 cm apart from the substrate holder, at a substrate temperature of about 300°C. The Se-deposition rate, measured by a quartz crystal monitor, was on the order of 0.5-0.8 μm/sec. The substrate was indirectly heated up using the Joule-effect with a Mo thin sheet. In this way a substrate temperature of

400-500°C could be reached in less than one minute. One of the problems encountered with the selenization of elemental layers was the sticking of the formed CuInSe_2 film. If the In layer was deposited on top of Cu layer at a substrate temperature below 100°C the sticking was very poor. The best adhesion was obtained when the In layer was deposited at a substrate temperature close to its melting point. It seems that at this temperature Cu and In mix completely [28]. After the selenization process, the CuInSe_2 film was polycrystalline with a grain size larger than 1 micron and it was very well oriented along the (112) direction. The $\text{CuInSe}_2/\text{CdS}$ solar cells were made following the method described above. The best cells prepared with this technique gave the following photovoltaic parameters: $V_{oc} = 380 \text{ mV}$, $J_{sc} = 39 \text{ mA/cm}^2$, $f.f. = 0.61$, $\eta = 9.1\%$

The conclusion of this work was that the selenization of elemental Cu-In layers seemed to be a very good technique to make CuInSe_2 films for the following three reasons:

- a. it is a scalable technique.
- b. it allows the formation of well-crystallized and single phase CuInSe_2 layers over large areas.
- c. Se-vapor in the selenization process works as well as H_2Se .

It was evident that in order to improve the performance of the cells it was necessary to add Ga to the precursor. In this way a $\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ film as the absorber material is obtained. Since the sputtering technique didn't allow Ga to be deposited directly, the deposition of the precursor was carried out by high vacuum evaporation assisted by an electron beam gun (E.B.G.). The Cu, Ga and In elemental layers were deposited by E.B.G. evaporation from a single rotatable crucible, in order to have a good uniformity on the substrate. First of all, 370 nm of In and 240 nm of Cu were deposited in sequence on top of a Mo covered glass substrate, which was kept at 120°C. Then the In-Cu bilayer was annealed at 290°C for 30-60 min in order to form the $\text{Cu}_{11}\text{In}_9$ phase. After the annealing, 120 nm of Ga were deposited at 240°C substrate temperature. At this temperature Ga reacts with the $\text{Cu}_{11}\text{In}_9$ phase forming the CuGa_2 phase and freeing a small amount of In. A substrate temperature of 240°C was chosen for the deposition of Ga since the CuGa_2 phase melts at 254°C. It had been confirmed by X-ray diffraction that the Cu-Ga-In film was made up of the $\text{Cu}_{11}\text{In}_9$ phase, the CuGa_2 phase and a small amount of In. This method for preparing the Cu-Ga-In elemental layers gives the maximum possible intermixing between the layers, without having melt droplets in the film. Since the addition of Ga, being a low-melting element, increases the amount of liquid present in the film at a given temperature, a new selenization process was implemented. A peculiarity of this process was the oscillation of the substrate temperature at the first stage of CuGaInSe_2 growth. The temperature oscillation seemed to be very effective in containing the surface tension of the liquid. At the beginning, the substrate temperature was raised up to 280°C in about 30 s and decreased to 200°C in about 3-4 min. During this first oscillation a small part of the film grew on the surface. This covering seemed to be sufficient to contain the surface tension during the second oscillation up to 450°C, which was done with a rise time of about 1 min and a cooling down time of about 6 min. During the second oscillation part of the film grew further covering the film with a solid one. Hence allowing a

third temperature oscillation and so on. It has been seen that the process depends on both the oscillation rise time, which should not be larger than 2 min for reaching a maximum temperature of 550°C and the cooling down time from 550°C to 200°C which should be between 6 to 9 min.

At this stage, the front-contact was also changed; 30-50 nm thick layer of intrinsic CdS at 220°C substrate temperature was deposited by sputtering on top of the CuGa_{0.3}In_{0.7}Se₂ films. The cell was completed with a 1-2 μm thick film of In-doped CdS or Al-doped ZnO, deposited by sputtering. On average, better results were obtained when soda lime glass was used as a substrate, indicating that the diffusion of Na atoms into the growing CuGa_{0.3}In_{0.7}Se₂ film during the selenization step, should play some role. These cells shown a maximum efficiency of 12.4% with an open-circuit voltage of 450 mV, a short-circuit current density of 40 mA/cm² and a fill factor of 0.69. No better efficiencies were achieved because this process doesn't allow a Ga concentration gradient to be obtained within the film thickness. Probably, if the junction was made with a thin layer of CdS obtained by chemical bath deposition, a larger efficiency could be achieved [29]. For this reason new type of precursors were tested, which allowed the concentration profile of Ga to be easily designed[30].

As it was the custom at that time, a substrate of 1 inch², 4mm thick soda-lime glass was used. The substrate was mounted in a sputtering chamber, where 4 targets namely Mo, In₂Se₃, Cu and a Cu-Ga alloy containing 50% at. of Ga and 50% at. of Cu were installed [31, 32]. Common commercial suppliers provided Mo, Cu and the Cu-Ga alloy, while the In₂Se₃ target was home-prepared, starting from the In and Se elements. In and Se elements were put in a suitable graphite container and brought to a temperature higher than the In₂Se₃ melting point (890°C) and then slowly cooled down to room temperature. This process was done in an oven where an inert gas such as N₂ was introduced at a pressure higher than 10 atmospheres in order to avoid the In or Se evaporation. The target was polycrystalline and exhibited a 99.9% density comparable with the bulk material.

This characteristic of the target is very important since, if a target prepared by "hot pressing" starting from In₂Se₃ powder was used one could have instabilities in the sputtering discharge produced by the high vapor pressure of Se.

Furthermore, if the cooling of the target is not very effective, some cracks at the edges of the target can form. On top of the soda-lime glass, 1 μm of Mo, 1.5 μm of In₂Se₃ and 0.2 μm of Cu were deposited in sequence at room temperature by sputtering. Mo and Cu were deposited by pulsed D.C. sputtering while, In₂Se₃ was deposited by R.F. sputtering.

The Mo-In₂Se₃-Cu stacked layers were brought to a temperature of 450°C where they were left to interact, respecting their phase diagram, for about 30 min. In this way a film of CuInSe₂ was formed. As it can be seen in figure 5(a), this layer contains a residual of the Cu₁₁In₉ and In₂Se₃ phases.

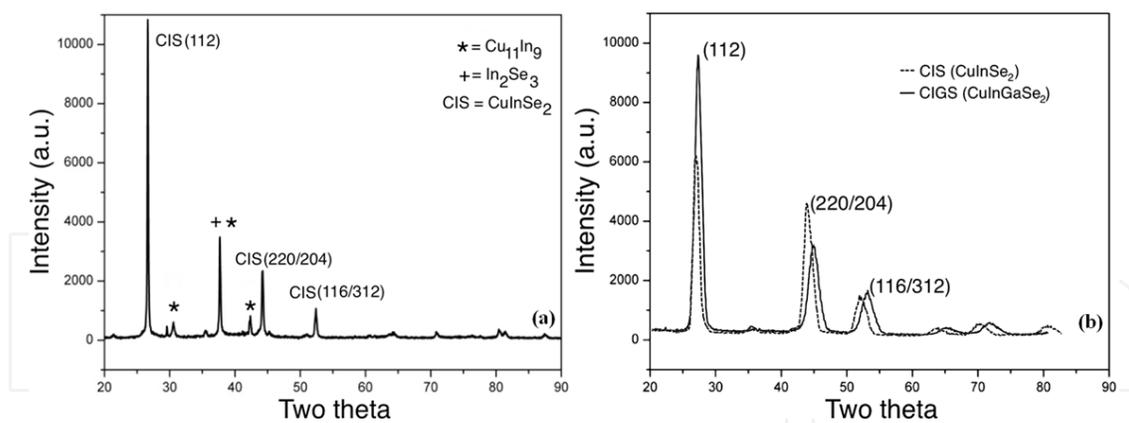


Figure 5. a) CuInSe₂ precursor X-Ray Diffraction spectrum. (b) Comparison between CuInSe₂ (dashed-line) and CuInGaSe₂ (solid-line) X-Ray Diffraction spectra.

In order to obtain the right CuInSe₂ film without any secondary phases, the precursor had to be selenized at a substrate temperature of 520–530°C. The selenization was done in the same way described before. Similar technology was also reported by other authors [33] but InSe instead of In₂Se₃ was used and it was deposited by high vacuum evaporation (HVE).

Furthermore, the selenization was started from room temperature up to 500°C and then no precursor was formed before selenization. In order to make the Cu(In,Ga)Se₂ film, the CuInSe₂ layer, obtained as described before, was covered by 80 nm of the Cu-Ga alloy (50%-50%) deposited by D.C. sputtering and this system was again selenized. The Cu(In,Ga)Se₂ film, formed in this way has a graded Ga content, that means it contains more Ga close to the surface than into the bulk. The Cu(In,Ga)Se₂, analyzed by X-rays, exhibits the peaks of Cu(In,Ga)Se₂ material as one can see from figure 5(b) where the diffraction peaks are shifted to higher angles with respect to CuInSe₂.

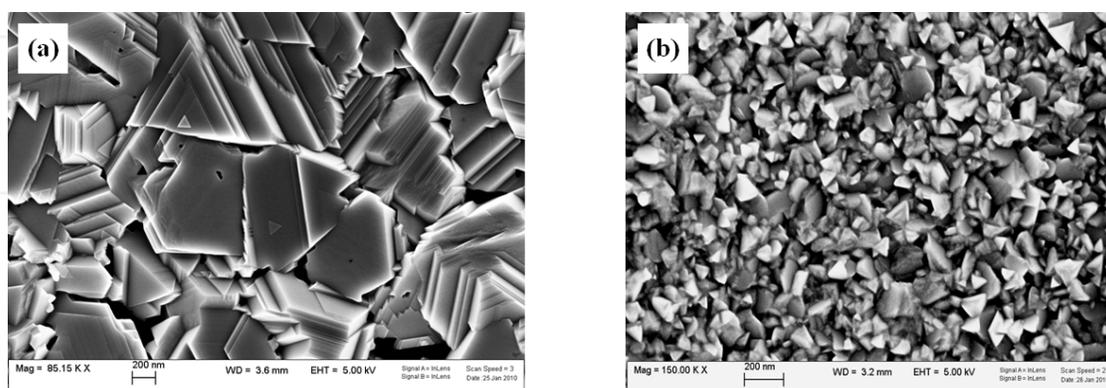


Figure 6. a) CuInSe₂ film surface morphology after selenization. (b) CuInGaSe₂ film surface morphology after selenization.

Figure 6(a) shows the morphology of the CuInSe₂ film while figure 6(b) displays the morphology of the Cu(In,Ga)Se₂ film referred to the two-steps process presented in figure 7. In

order to have a better control on the Ga concentration gradient of the CuInGaSe₂ film, the THiFiLab developed an alternative way to prepare the precursor (see figure 7).

Once the CuInSe₂ precursor is obtained it is possible to follow two different pathways:

1. The process continues by depositing in sequence on top of the precursor, formed by CuInSe₂+Cu₁₁In₉ and In₂Se₃ as described before, a film of Ga₂Se₃ followed by a film of Cu at a substrate temperature of 400-450°C. This new precursor is then selenized in pure Se vapor and the Cu(In,Ga)Se₂ film is obtained.
2. The precursor is immediately selenized and on top of the so-obtained CuInSe₂ film, the same sequence of Ga₂Se₃ film followed by a Cu film is deposited at a substrate temperature of 400-450°C. This system is suitable for the selenization process and a film of Cu(In,Ga)Se₂ is made.

With this second method we have more freedom in varying the concentration profile of Ga in the final Cu(In,Ga)Se₂ film since the profile depends on the ratio between the Ga₂Se₃ and CuInSe₂ film thicknesses. In contrast, the first method is more convenient because it needs only one selenization step. In Table 3 the results of manufactured cells with both methods are summarized.

Great improvements have been made in finishing the cell, in fact Cu(In,Ga)Se₂/CdS solar cells were prepared as described above, by depositing in sequence on top of Cu(In,Ga)Se₂ layer, 60 nm of CdS(F) [34], 80 nm of pure ZnO and 1µm of ZnO doped with 2% atomic of Al.

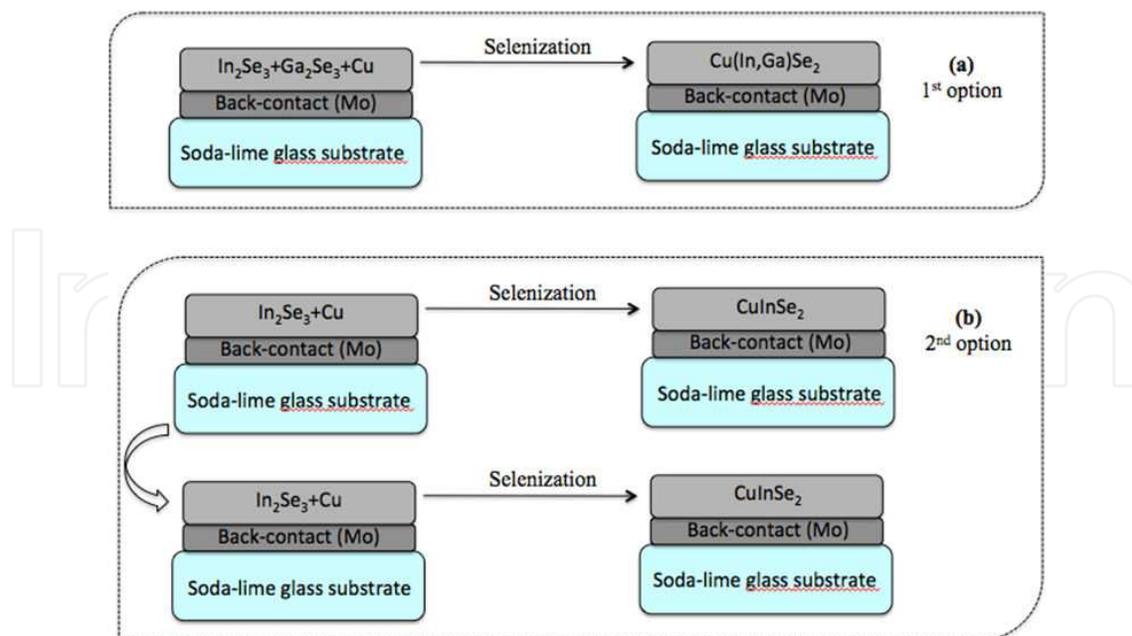


Figure 7. Representation of the two options developed in the THIFILAB, University of Parma-Italy to obtain high quality Cu(In,Ga)Se₂ absorber film. (a) single-step process. (b) double-step process. For both options all the layers are deposited by sputtering and selenization in pure Se atmosphere is made.

If one uses the sputtering technique for the deposition of CdS films, employed as the window material in Cu(In,Ga)Se₂ based solar cells, great results are not obtained and efficiencies converge to values not higher than 13% -14%. This result is due to the fact that these devices exhibit a too high diode reverse saturation current. One possible explanation is that the grain boundaries in the CdS film are active and can channel the diode reverse current.

Absorber	Ga/In+Ga (%)	Voc (mV)	Jsc (mA/cm ²)	FF (%)	Efficiency (%)
CuInSe ₂	0	410	39.8	70.20	11.45
Cu(In,Ga)Se ₂	20	531	34.8	71.60	13.23
Cu(In,Ga)Se ₂	20	578	35.2	71.08	14.46

Table 3. Photovoltaic parameters of the solar cells fabricated by sputtering and selenization in pure Se atmosphere.

It is possible to get over this problem by introducing in the sputtering chamber, during the CdS deposition, Argon containing 3% of CHF₃. This gas is decomposed and ionized in the sputtering discharge, freeing F⁻ ions which, being strongly electronegative, are directed to the substrate that is the positive electrode; here two different events can happen:

- 1- the presence of energetic F⁻ ions near the substrate favors the formation of a fluorine compound such as CdF₂ during the growth of the CdS film [34].
- 2- the F⁻ ions, accelerated by the electric field present in the discharge, hit the film surface during the deposition with sufficient energy to sputter back the more weakly bonded Cd or S atoms.

This effect leaves a CdS film with high optical quality and structural properties. We can see in figure 8 that the CdS films deposited in Argon+CHF₃ have an energy gap greater than that of the films deposited in Argon alone. Better efficiencies (15%-18%) are routinely obtained if CdS(F) films are used. One can explain this fact by considering that CdS(F) may contain CdF₂ probably segregated in the grain boundaries and this can be useful to passivate them.

As an alternative to ZnO(Al), 0.5 μm of ITO doped with Zr was used. All the layers were deposited by sputtering. While CdS(F) and pure ZnO were deposited by R.F., ZnO(Al) and ITO(Zr) were deposited by pulsed D.C. sputtering. ITO doped with Zr has been used since it was discovered that for dielectric oxides, permittivity can be increased by the addition of higher-permittivity oxides such as ZrO₂ (or HfO₂). It is also known that the permittivity of dielectric oxides increases rapidly with even small additions of a higher-permittivity constituent and this is especially true for high-frequency permittivity ε_∞. The increase in ε_∞ as Zr is added can shift λ_p, which corresponds to the plasma resonance wavelength, to a longer wavelength and make it possible to improve NIR transmission significantly without altering the material parameters, like carrier concentration or mobility[35].

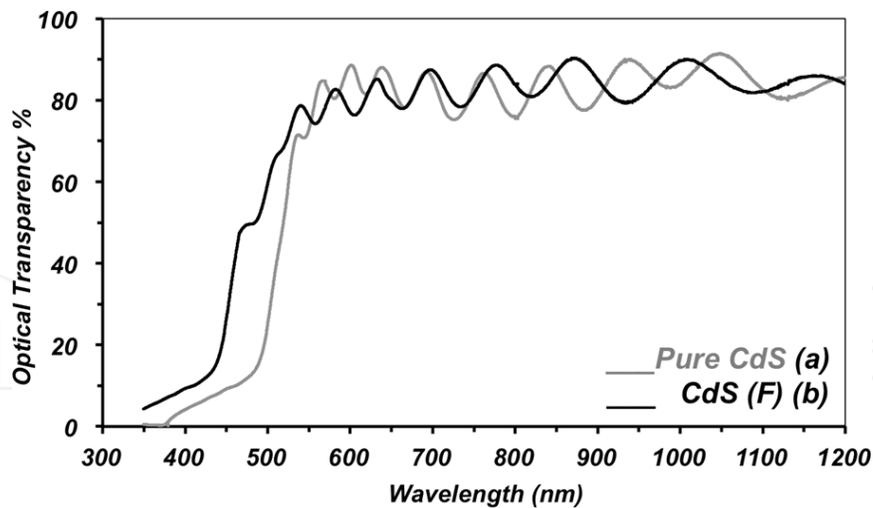


Figure 8. Transmission spectrum of an 80 nm thick sputtered CdS film: (a) deposited in pure Argon and (b) deposited in Argon+CHF₃. The shift of the absorption edge towards shorter wavelengths proves the beneficial effects of deposition in the presence of CHF₃. Redrawn from "Proceedings of 3rd World Conference on Photovoltaic Energy Conversion, 2003, Osaka, Japan, May18-21, Vol 1, 469 – 470.

In order to further improve the efficiency of the solar cells, the precursor was further modified by replacing In₂Se₃ and Ga₂Se₃ with InSe and GaSe targets. The change in the starting selenides was especially effective as it resulted in the complete mixing of the materials, which formed the precursor. In fact, at a given temperature, InSe and GaSe were more reactive with Cu than their counter parts In₂Se₃ and Ga₂Se₃. So we came to the last version of the fabrication process for the CIGS-based solar cells developed so far at the ThiFiLab.

The starting system was the usual sputtering machine in which 4 targets namely Mo, InSe, GaSe and Cu were contained. While Mo and Cu were deposited by pulsed-D.C., InSe and GaSe were deposited by R.F. sputtering. The construction of the solar cell began with the deposition of a Mo bi-layer at room temperature. The first Mo layer was quite thin, 30 nm and was deposited with an Ar flow of 45 sccm, which corresponds to a pressure of 4.5x 10⁻³ mbar. The Ar flow was then decreased to 15 sccm, which corresponds to a pressure of 1.5x 10⁻³ mbar.

Approximately 500 nm of Mo was deposited. The deposition of a bi-layer of Mo was necessary in order to have good adhesion of the Mo film to the substrate [36].

In order to get a good precursor, it was discovered that the sequence of InSe, GaSe and Cu as well as the substrate temperature at which they were deposited was very important. While Mo films had to be deposited at room temperature for sticking purposes, both InSe and GaSe layers were deposited at a high temperature (400°C) in order to avoid a Se-excess growth. The thickness of the InSe film was commonly 1.5 μm and that of GaSe was 0.5 μm. Cu was also deposited at a substrate temperature of 400°C and its thickness was around 350 nm. All the layers mix during the deposition and don't require further annealing. An X-ray analysis shows that the precursor exhibits a mix of InSe, GaSe and CuInSe₂ phases (figure 9a), while, the selenized material shows two phases one which contains 30% of Ga and the other one which contains 60% of Ga (figure 9b).

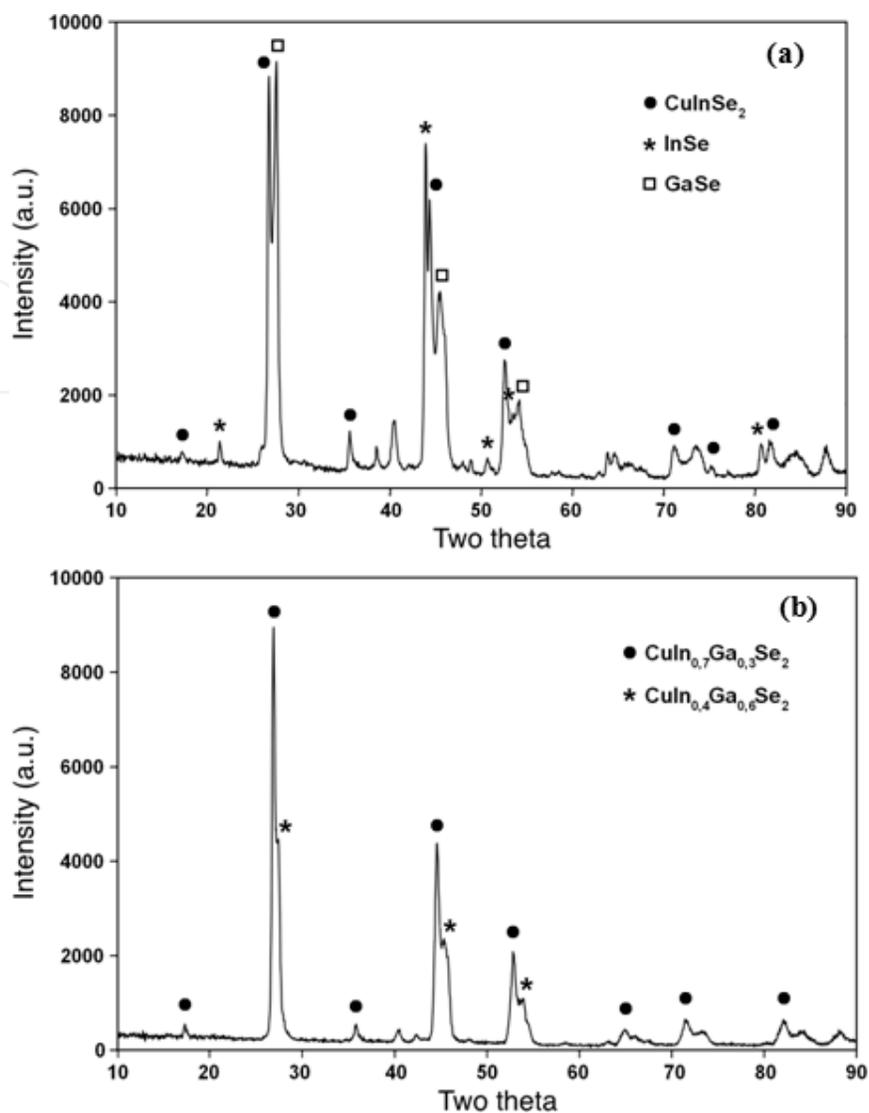


Figure 9. Cu(In,Ga)Se₂ precursor X-Ray Diffraction spectra (a) before and (b) after selenization.

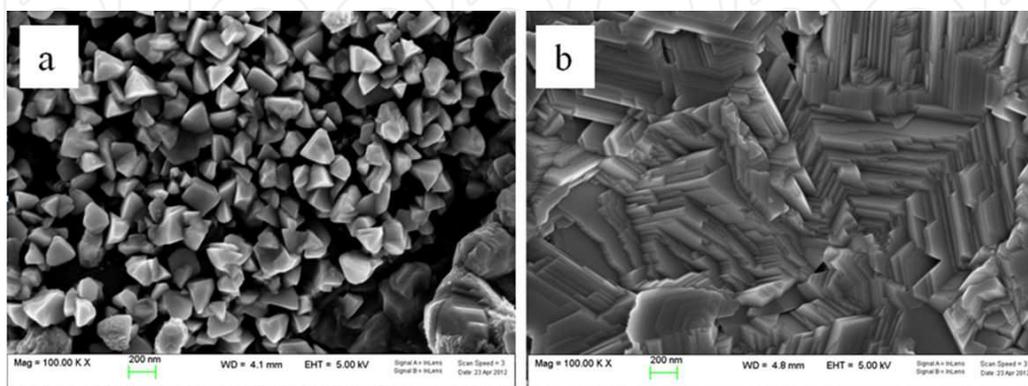


Figure 10. Electron microscope image of precursor (a) before and (b) after selenization.

The precursor is then selenized in a vacuum chamber where pure Se is evaporated from a graphite crucible. Selenization lasts approximately 7 minutes. The first 5 minutes are used to bring the substrate from room temperature to 530°C and the last 2 minutes are spent by leaving the substrate at 530°C. The morphology of the precursor before and after selenization is shown in figure 10.

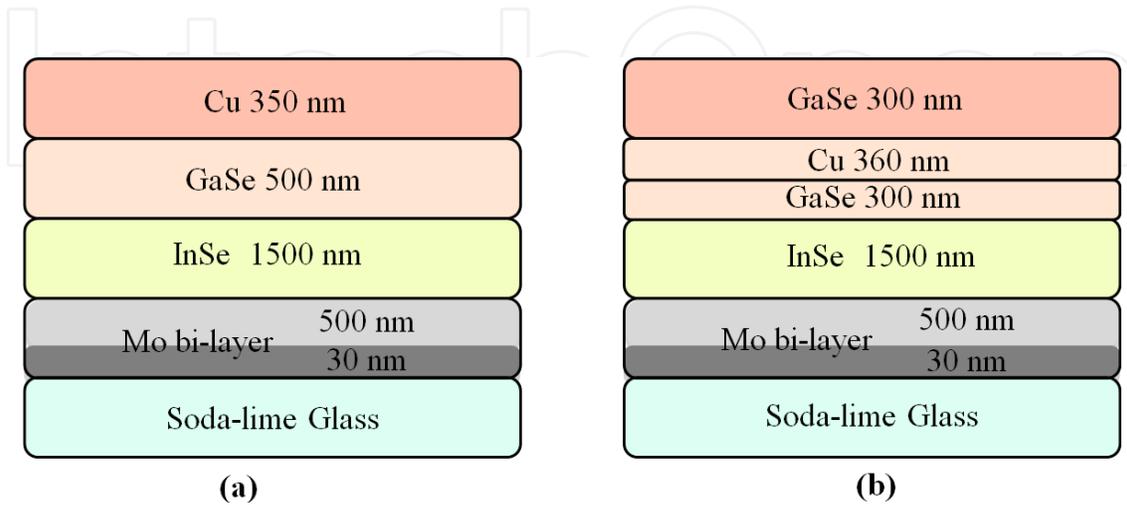


Figure 11. Preparation of the precursor. (a) Sequence of deposition for the InSe, GaSe and Cu layers; (b) the last new optimized sequence for the InSe, GaSe and Cu layers, which led to a high efficiency CIGS-based solar cell.

The cell was completed by depositing the CdS layer, the transparent electrode and the contact grid in the same way that was previously described.

Solar cells made in this way exhibit an efficiency of about 13% with an open circuit voltage (V_{OC}) that is never higher than 500 mV, a high short circuit current density (J_{SC}) on the order of 40 mA/cm² and a f.f. of 0.62-0.65.

The low open circuit voltage and f.f. are attributed to the fact that Ga, being less reactive than In, tends to diffuse to the bottom leaving the surface poor in Ga. This has been confirmed by doing a depth profile, in which one can see that most of Ga is confined to the bottom. At this point, in order to have more Ga close to the surface, a final change in the sequence of the layers had been performed and is highlighted in figure 11.

A GaSe thin layer is put on top of Cu and another layer of GaSe is put under Cu on top of InSe. The new precursor has been selenized in the same way as the old precursor. A depth profile made on this new absorber shows that there is more Ga close to the surface and that it decreases starting from the surface and increases again going deep into the sample (figure 12). The characteristics of the solar cells made with the new absorber exhibit a V_{OC} close to 570 mV, a J_{SC} of ~38 mA/cm² and f.f. of 0.74 with an efficiency of 16.2% (figure 13).

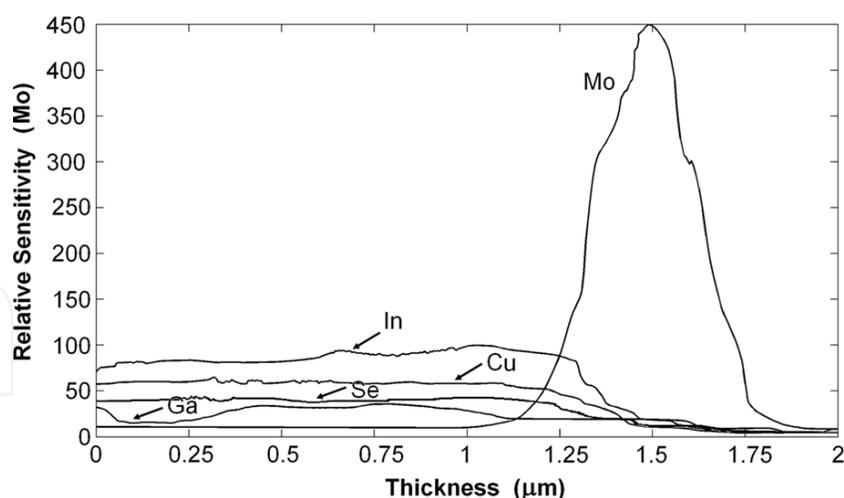


Figure 12. Sims depth profile of a CIGS film obtained starting from the new stratigraphy of the InSe/GaGe-based precursor. Note the trend of the Ga profile, which decreases starting from the surface and then re-increase approaching the back contact.

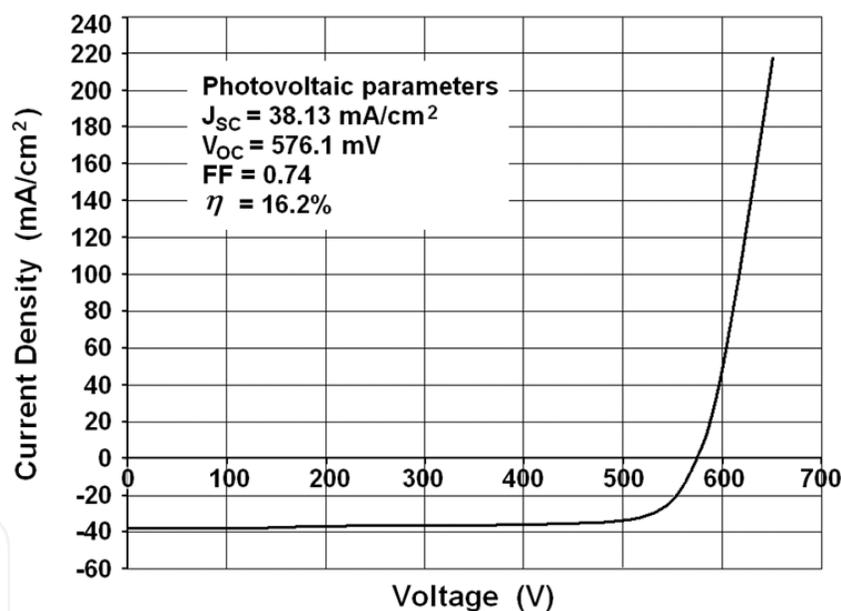


Figure 13. J-V characteristics of the Cu(In,Ga)Se₂ based solar cell made with the new precursor.

The process described above was also used to prepare Cu(In,Ga)Se₂/CdS solar cells directly on ceramic substrates (commercial tiles). This kind of ceramics is normally used in construction of buildings aimed to energy savings through the implementation of ventilated walls. However, the ceramic tile was modified in order to adapt its surface to become a good substrate for PV purpose. For this reason the surface of the tile was vitrified with the application of a special enamel. By checking in detail the composition and the constituent elements of this layer it has been possible to make the ceramic very similar, from the physico-chemi-

cal point of view, to the most common soda-lime glass. In fact, solar cells prepared on this ceramic substrate exhibit similar results to those obtained by using soda-lime glass as a substrate. (see figure 14 and table 4)

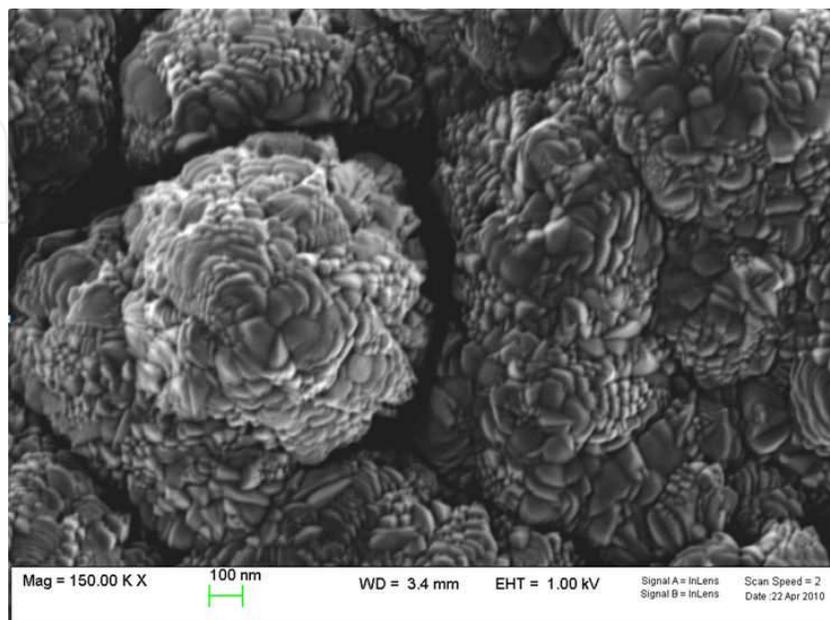


Figure 14. Scanning electron microscope photograph of the surface morphology of a CIGS film grown on an evolved ceramic tile.

Absorber	Ga/In+Ga (%)	Voc (mV)	Jsc (mA/cm ²)	FF (%)	Efficiency (%)
*Cu(In,Ga)Se ₂	10-15	531	34.8	71.60	13.23
#Cu(In,Ga)Se ₂	15-25	570	38	74	16.02
^Cu(In,Ga)Se ₂	15-25	577	36.4	72	15.12

Table 4. Photovoltaic parameters of CIGS-based solar cells fabricated by using the last two different precursors both on soda-lime glass and commercial ceramic tile substrates. *the absorber layer is made starting with the In₂Se₃+Ga₂Se₃+Cu precursor and the cell is realized on SLG. # the absorber layer is made starting with the InSe+GaSe+Cu+GaSe precursor and the cell is realized on SLG. ^the absorber layer is made starting with the InSe+GaSe+Cu+GaSe precursor and the cell is realized on commercial ceramic tile.

4. A future perspective: the Cu₂ZnSnS₄ system

Since it is necessary to develop non-Si-based solar cells due to a lack of highly pure Si sources, the PV world is oriented to develop new type of solar cell material that uses simple process and low-cost easily scalable techniques. Thin film polycrystalline solar cells have shown a remarkable growth in terms of efficiency, stability and scalability. CdTe and CuInGaSe₂ (CIGS) materials have demonstrated to be robust and reliable for delivering low cost

solar electricity. Because of direct band gap, which assures a high absorption coefficient, these devices use a very limited amount of material, which strongly reduces the production costs. However some issues on this are raised in particular the presence of rare and toxic elements that could impact on the perception of the population.

Indium and gallium for CIGS and tellurium for CdTe result to be rare materials that could limit the module production when we talk about Terawatts, if a proper recycling system is not set up [37].

Moreover, there is an old controversial discussion on the opportunity of using cadmium in photovoltaics; unfortunately this argument has been going above the scientific considerations and has been taken as an opportunity for crystalline silicon producer to limit the spreading of less expensive polycrystalline thin film devices [38].

As a matter of fact the introduction of cadmium in photovoltaic materials has been in the fabrication either of CdTe absorber material or of CdS buffer layer; in the first case there is mainly a problem or perception since CdTe is a secure and non toxic material, in the second case the amount of material is very little and encapsulated and the impact of cadmium in the overall environmental effect is minimal.

However, to overcome the environmental issues and most important to remove any doubt of massive production connected with material scarcity, in 1996 Katagiri et al. [39] have introduced a new device based on $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) absorber layer; the structure was very similar to the CIGS standard structure having CdS as buffer layer, ZnO as front and Mo as back contact. The idea was not new since it has been introduced for the first time in 1988 from Ito and Nagazawa by making a heterojunction between CZTS and CTO (Cadmium Tin Oxide) [40]. The introduction of CZTS allows practically to substitute indium and gallium with zinc and tin which are pretty much available on the earth crust.

Furthermore, thin film photovoltaics is competing with other industries, which use similar elements such as In (flat panel) and Ga (optoelectronics). This issue together with the raw material availability mentioned above could affect the raw material prices. As already written the availability of In could limit the module production in the terawatt/year range [37].

The advantage of the kesterite materials (CZTS family) is that with similar material properties, similar preparation methods and same device structure as chalcopyrite solar cells, they are a real alternative to In-containing absorbers.

Generally for kesterites two kind of absorbers are considered: $\text{Cu}_2\text{ZnSnS}_4$ and $\text{Cu}_2\text{ZnSnSe}_4$, however their structure is pretty different since in the first case we have a real kesterite structure (space group I4) and in the second case a stannite structure is observed (space group I₄2m).

So when it comes to a $\text{Cu}_2\text{ZnSn(S,Se)}_4$ absorber, which has also been employed, a polymorph structure has been observed. Polymorphism gives place to coexistence of different structure and it has been shown that stannite structure has lower binding energy and so lower stability. Stannite structure has lower band gaps and this could explain the lower open circuit voltages of these devices compared to the expected values. Band gap of the materials are

fluctuating depending on the different deposition methods and crystallization procedure; however most of band gaps for Cu₂ZnSnS₄ are around 1.5eV [41-46] while for Cu₂ZnSnSe₄ they stay around 1 eV. The main reason for the fluctuation of the band gaps is the very likely presence of secondary phases. As a matter of fact CZTS materials tend to produce many secondary phases, investigation on the phase diagram of this material shows that only in a very small region is possible to make single phase CZTS while a large variety of different secondary phases can easily be formed, such as ZnS(e), CuS(e), CuSnS(e). However the best solar cells show a Zn-rich and Cu-poor composition, which tendentially provides a ZnS(e) secondary phase. While ZnS(e), having a wide band gap and low conductivity, would not affect the open-circuit voltage, it could be responsible for the high series resistance observed in all solar cells [47,48].

The standard structure of the solar cells is very similar to the CIGS one, using ZnO doped with aluminum as front contact, CdS as buffer layer and Molybdenum as back contact. Friedlmeier et al. introduced this first design in 1997; they fabricated thin film solar cells by using a CZTS layer as the light absorber in contact with an n-CdS/ZnO window layer [47]. The best energy conversion efficiency produced by these cells was 2.3%. Later, Katagiri's group broke this record in 1999 producing a CZTS solar cell with 2.63% power conversion efficiency. In this cell, the CZTS film was deposited on a Mo coated soda lime glass (SLG) substrate [42]. By optimization of the sulfurization process, the efficiency of the solar cells was increased to 5.45% in 2003 [49], and then to 6.7% in 2008 [50].

Finally in 2010 Todorov reached 9.6% by inserting a selenization step [51], in 2011 the psychological limit of 10% has been overcome by Mitzi et al. by a non vacuum deposition method [52].

CZTS has been prepared already by a wide variety of deposition methods with different results, however what is surprisingly remarkable is that both vacuum and non vacuum techniques are very much in competition on the efficiency level. This is not the case for other polycrystalline thin films where generally the vacuum techniques are delivering higher performance. A large number of different vacuum deposition methods have been employed.

Vacuum-based fabrication techniques normally involve deposition of the constituent atoms of the CZTS compound on a substrate by sputtering or evaporation/coevaporation of the target sources under a certain pressure and temperature. These techniques have the advantage of easily controlling the chemical composition and phase profile in the thin films and normally have good reproducibility.

As mentioned before the first CZTS processing by Ito and Nakazawa was made by vacuum deposition, such as atomic beam sputtering in 1988. They were able to measure a band gap of 1.45 eV and the photovoltaic effect was proved by preparing an heterojunction with cadmium tin oxide (CTO) and a voltage of 165 mV was obtained [40].

After a long time in 1996 Katagiri made a complete photovoltaic cell with the following structure: ZnO:Al/CdS/CZTS/Mo/SLG. The absorber layer was deposited by electron beam gun followed by sulfurization; this process gave a power conversion efficiency of 0.66%. In 1997 Friedlmeier et al. at the university of Stuttgart deposited the CZTS absorber layer by coevaporation of the single constituents (using a similar method as the CIGS fabrication

process where the single elements or binary chalcogenides compounds are vacuum-deposited onto a heated substrate) obtaining a 2.3% efficiency cell. They also report, for the first time, that the electrical resistivity of the films can be improved considerably by treating the films with a KCN solution; this is still an important step of the fabrication process. Later on, Katagiri improved his deposition process by substituting Zn with ZnS in the e-beam sequence and improved the adhesion of the absorber to the molybdenum, increasing its efficiency up to 1.08%.

An approach based on one-step synthesis of CZTS thin films by simultaneous coevaporation of precursor sources Cu, Zn, Sn, S was reported by Tanaka et al. The grain size of the film depended on the substrate temperature. Larger grains were obtained at higher substrate temperature [52].

An integrated vacuum apparatus, which combined the RF sputtering technique with the sulfurization process was employed to reduce the effect of moisture from air ambient on the property of CZTS films. Target sources were based on ZnS, SnS and Cu. Both the quality and reproducibility of the CZTS films were significantly improved by this method and a 5.7% conversion efficiency with the CZTS-based thin film solar cells was achieved [53]. By eliminating the metal oxide impurity in the CZTS films using deionized water, the efficiency of the solar cells was further improved to 6.7% [49,54].

A lot of work has been recently presented by the IBM group; the research has been going on two different paths: vacuum and non vacuum deposition of CZTS.

For vacuum deposition a recent work from Wang et al. has been presented where the single elements are contemporarily evaporated on a SLG substrate by a rapid thermal deposition system. With an absorber thickness of only 1 micron and a few minutes annealing time the process is very promising for industrial application and has demonstrated a 6.8% conversion efficiency. High series resistance and a high charge recombination limit the efficiency [55].

Generally, if the composition of the precursor films is copper rich, it results in the formation of a Cu_{2-x}S secondary phase, which can be removed by a post treating with KCN aqueous solution.

In metallic layer deposition it has been shown that the sequence of the different elements plays an important role in the crystallization of the absorber as shown with controversial results by Araki et al. [56] and Fernandes et al. [43] by pulsed laser deposition.

Another important effect is the known loss of Sn in CZTS during the annealing process. Above 350°C Sn tends to re-evaporate and stoichiometry is lost. Different corrections of this effect have been presented among which the addition of inert gas in the chamber during the annealing or addition of SnS in the precursor to compensate the loss.

Weber et al. studied the loss of Sn in CZTS during the annealing process. It was found that desorption of SnS from the CZTS at temperature above 350°C led to the losses of Sn in vacuum. The decomposition process of CZTS could be reduced by addition of an inert gas in the chamber where the sintering was carried out [44]. Redinger et al. suggested to add extra SnS and S materials in the precursor to prevent the decomposition of CZTS at high temperature [45].

Non vacuum deposition methods are very attractive since they would allow a lower production cost since expensive vacuum machines and high energy evaporation system would be avoided.

Like CdTe and CIGS also CZTS has been prepared by non-vacuum alternative methods such as spray pyrolysis, electrochemical deposition, and spin coating of precursor solutions, but in this case with very nice performance [48].

One of the first non vacuum synthesis of CZTS thin films by spray pyrolysis of precursor solutions was introduced in 1997 by Nakayama and Ito. The layer was fabricated by preparing a mixture of water and ethanol with specific precursors such as CuCl, ZnCl₂, SnCl₄, and thiourea. With different precursors many other laboratories have studied this simple fabrication method, like Kumar et al. (high substrate temperature spray) [57] and Prabhakar et al. (ultrasonic spray) [58].

Spin-Coating of CZTS precursor solution is one of the most successful technique among the non vacuum methods but also among the vacuum ones. It is typically consisting in first the preparation of a precursor solution, then spin-coating the precursor solution on a SLG substrate and finally annealing the stacks in a controlled atmosphere to form the CZTS absorber.

Many different recipes have been presented from different researchers like Tanaka et al. [53], who presented an all-non vacuum deposited device. With a copper poor solution a 2.03% efficiency has been obtained. Other researcher like Pawar improved the crystallinity by the introduction of a complexing agent which increased inhomogeneity on the surface, later improved by sulfurization [59]. Fischereder et al. deposited CZTS films by spin coating a precursor solution consisting of metal salts of copper (I), tin (IV), and zinc (II) and thioacetamide in pyridine. They found out that the formation of CZTS compound occurred at temperature as low as 105°C in vacuum. The band gap energy of the films varied between from 1.41 to 1.81 eV by changing the annealing temperature point [60]. This is probably due to the coexistence of secondary phases in the film under low annealing temperature. Todorov et al. firstly presented best efficiency by preparing a CZTS solution based on hydrazine. The CZTS films were obtained by annealing the precursor films in sulfur or sulfur and selenium atmosphere at high temperature. The best cell efficiency was 9.66%, later improved by Mitzi et al. up to 10.1%. These devices use a hybrid absorber which is selenized and sulfurized as well. Measurements presented and comparison with a typical high efficiency CIGS solar cell shows that this high performing device still suffers from dominant interface recombination, short minority carrier lifetime, and high series resistance.

In conclusions, CZTS is a new material, which has in the last ten years seen a huge improvement; a lot has been done to study the physical properties and to control the stoichiometry, especially secondary phases that are still a strong limitation to high efficiency. High series resistance and short minority carrier lifetime generally reduce the current of these devices and the tendency to form a great numbers of detrimental defects decreases the open circuit voltage.

However efficiencies above 10% have been demonstrated, moreover these devices can be successfully prepared in a very large variety of deposition methods from vacuum growth

(coevaporation, sputtering, electron beam of precursors) to non-vacuum techniques among which the record cell has been obtained.

5. Conclusions

The need for more and more energy supplies due to increased demand from emerging countries such as India, China and Brazil and the contemporary necessity to preserve the environment, has increased interest in the development of new technologies that make use of solar energy.

In particular photovoltaic solar energy, the direct conversion of solar energy into electricity by means of semiconducting materials, has had very strong development in the last 20 years.

The most important parameter that characterizes a photovoltaic device is the ratio between its conversion efficiency and its cost. A value less than 0.5 \$/W_p is considered competitive with the electricity obtained from fossil energy sources (Grid-parity). Although large progress in Cu(In,Ga)Se₂ solar cell scientific knowledge and process management has been accomplished, as evidenced by the high module and cell efficiencies fabricated by many groups, the range of deposition and device options that have been developed are not sufficient to ensure the achievement of this objective. In particular, for CIGS-based devices the question is: what is needed to be done to guarantee that Cu(In,Ga)Se₂ solar cell technology reaches its potential for large-scale production?

We could first respond by indicating how critical the need is for opportunities to develop new production technologies, including enhanced equipment for the deposition of the layers as well as production processes based on well-known engineering models. In addition a new second generation of production process-control tools will have to be worked out.

Improved equipment and very good diagnostic can be directly turned in to higher throughput, yield, and performance. This results in a better conversion efficiency-cost ratio.

In the ThiFiLab, considerable effort in the direction of simplifying the production process has been made and the achieved results suggest that we are closer to the development of a high-yield production line of low-cost highly efficient modules.

A second essential question could be: what might be the innovations that are needed for laying the groundwork for a new generation of thin-film Cu(InGa)Se₂-based solar cells?

A lot of R&D can be made by studying alternative substrates such as the ceramic tiles proposed by the ThiFiLab that directly allow the buildings integration of photovoltaics (BIPV).

Another step may be achieved by developing low-temperature manufacturing processes that allows the use of innovative substrates such as polymeric ribbons, which represents a basic passage towards the low-cost Roll-to-Roll (R2R) technology. Similarly, there may be significant cost and processing advantages to a cell structure that enables the use of a Cu(In-Ga)Se₂ layer much less than 1 μm.

R&D on Cu(In,Ga)Se₂ remains very attractive as well as promising through all of these challenges, aimed at improving the knowledge of both the material and the device, in addition to developing new production technologies and revolutionary innovations.

The great stability over time shown by the high-efficiency devices together with the great variability of material stoichiometry and manufacturing processes provide a great expectation that this material will give its contribution to energy demand at a competitive price while respecting the environment.

In this groove the research on kesterites is to be placed; these are relatively new materials for solar cell applications, and a lot of research remains to be done before the best components and processing methods are found. In particular, concerning Cu₂ZnSnSe₄ as PV material a big effort must be made in the knowledge related to the segregation of phases, which affects the final functioning of the device. The structure of this cell, being similar to that normally used for CIGS solar cells, has already been well defined, but the deposition methods of the absorber layer are still subject of study. Despite this, with this material as absorber, solar cells with conversion efficiency greater than 10% have been realized.

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