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# Science and Technology of Innovative Materials

# Cycle 25

# Technological processes for CIGS based solar cells

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#### Abstract

The solar photovoltaics (PV) market has been booming since the late 1990's with an impressive 40% average annual growth rate and rapid growth has continued even in the last four years despite the bottlenecks in silicon feedstock availability. , which have determined a slow down in the decline of PV module prices. As an economic alternative to silicon a great deal of attention has been devoted to Cu(In<sub>x</sub>Ga<sub>1-x</sub>)Se<sub>2</sub> (CIGS) thin film based solar cells, whose development lead to demonstrate in 2010 a record efficiency of 20.3% on a 0.5 cm<sup>2</sup> laboratory cell.

The activity discussed in this thesis was performed in the frame of PED4PV project ("Industria 2015" programme of the Italian Ministry of Economic Development) aiming at the low cost production of thin film CIGS-based solar cells on conventional glass substrates as well as on alternative substrates suitable for building integration (such as ceramic and cement tiles) by using the relatively new, highly efficient, but yet largely unexplored technology called "Pulsed electron deposition".

This thesis reports about the set up of the technological processes that complement PED growth of the multilayer structure in the fabrication of the solar cells and their characterization. In particular the optimization of the Mo back contact deposition by sputtering is detailed, and the activity devoted to support Marazzi S.p.a and CTG S.p.a. in the development of ceramic and cement substrates, respectively, is described. A relevant part of the work has been devoted to the characterization of the cells. Current-voltage, capacitance-voltage and infrared thermography measurements gave the PED group the feedbacks necessary to improve the multilayer structure properties up to achieve an efficiency of 15.5% on lab-scale solar cells completely prepared at IMEM by depositing CIGS from a stoichiometric quaternary target at low temperature (270  $^{\circ}$ C) and without any post-growth treatment.

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# Introduction

The first form of renewable energy dates back to 1767, when Horace-Benedict de Saussure fabricated the first solar collector, able to absorb heat energy, by covering an insulated box with three layers of glass. The photovoltaic (PV) effect was described for the first time by A. E. Becquerel in 1839. In detail, he observed that a silver-chloride electrode immersed into an acidic solution and connected by a metal wire to a platinum electrode was able to generate a photocurrent upon illumination [1].

The discovery of photoconductivity in selenium, by Willoughby Smith in 1873, allowed the manufacturing by William Adams and Richard Day of the first solid-state photovoltaic device in 1876. Such device, based on the concept of the rectifying junction, was made of selenium crystal coated with platinum contact. Two decades later, in 1894, Charles Fritts used a thin layer of gold as electrical contact in place of platinum, obtaining in this way the so called Schottky barrier, able to favor the separation of the excitons formed at the selenium/gold interface in elementary charges. For many years the photovoltaic effect did not gain the interest of researchers- Only after the Second World War, solar power equipments became popular, first in the USA, in consequence of the development of both good quality semiconductor wafers and reliable methods aimed at manufacturing p-n junctions for applications in solid state electronics. From then on, there was a huge demand of solar energy equipment that brought to the manufacturing of the first solar cell based on silicon wafer, designed and fabricated in 1954 by Bell Labs by Pearson, Chapin, and Fuller, showing a conversion efficiency of about 6%. The year after, Western Electric began to sell commercial licenses for silicon PV technologies, but an estimated cost of ~\$200 per Watt-peak (Wp) made these cells not commercially appealing on a large scale for many years. In 1958, since solar energy was exploited as power supply space exploration equipment such as satellites and space stations, novel semiconducting compounds such as gallium arsenide, indium phosphide,

cadmium selenide and cadmium telluride, were intensely studied for PV applications since their conversion efficiency resulted to be higher than that of silicon. This date corresponds to the beginning of commercial use of solar energy. During the period between 1959 and 1970 the major discussion was focused on the strategies aimed at optimizing the gain in efficiency of solar cells and the reduction of costs for their manufacturing. Up to that time, the efficiency of the solar cells was only 14% and, considering their high manufacturing cost, it was not still convenient to exploit solar power in place of conventional sources for the production of electricity. However in the 1970's, Exxon Corporation designed an efficient solar panel whose manufacturing cost was lower than that of the conventional solar cell architecture produced at that time. This was likely the major technological milestone reached in the history of renewable energy.

In the 1970s the energy crisis experienced by the western oil-dependent world, caused by the Arab-Israel Yom Kippur War of 1973 and the Iranian Revolution of 1979, led to a sudden growth of interest in alternative energy sources, attracting great funding for research and development in those application areas. Different strategies have been explored for producing photovoltaic devices. In particular, alternative materials such as polycrystalline and amorphous silicon have been studied, organics have been widely employed in order to study innovative PV devices and the device architectures have been optimized (e.g. use of thin films). Regarding to this latter aspect, other different architectures as tandem and multiple band gap structures have been developed in order to increase the photovoltaic efficiency. During the eighties there was the evolution of large scale solar energy plants. This evolution culminated with the development of the largest plant, able to produce more than 20 kilowatts, in 1999. During the last decade of 20<sup>th</sup> century, an enormous investment was made in utility-scale solar plants, also incurring often in some technical inconveniences. At present day, the largest solar energy plant ever built is the Golmud Solar Park in China, with a capacity of 200 MW. This record is arguably surpassed by India's

Gujarat Solar Park, a collection of solar farms spread in the Gujarat region able to produce a total capacity of 605 MW.

The current PV market consists of a range of technologies, including wafer-based silicon and a variety of thin-film technologies. These technologies have been classified into three main generations. The classification criteria base on their possible chronological future application. Currently, we are in the era of first generation photovoltaic technology (1G), well projected towards the near future third generation technology, being the second generation (2G) based on thin film technology under researchers' interest [2]. Figure 1 shows the theoretical maximum efficiency achievable by each PV generation as a function of the production cost projections, although both the efficiency and the cost values are obviously approximate.



Figure 1: Theoretical efficiency of the three PV generation vs the production cost projections. The horizontal lines represent the main theoretical efficiency limits [3].

On the other hand, the real efficiencies of the best research solar cell, from 1975 to 2010, are reported in figure 2. Here a famous graph, edited by the U.S. National



Renewable Energy Laboratory (NREL) shows evidently that the evolution of the different PV technologies leads to an optimization of the device properties.

Figure 2: Evolution of the maximum experimental efficiency obtained for several PV technologies, from 1975 up to our days [4].

The evolution of photovoltaics lies in decrease of production cost (\$/W), achievable by eliminating unnecessary production steps and superfluous materials in the manufacturing of solar cells. For this reason, great attention is focused on the fabrication and engineering of solar cells in the form of thin film layer based devices. The second generation solar cells are then based on single-junctions, avoiding thus material waste. The challenging task in the context of second generation solar cell manufacturing consists in maintaining the performance obtained by solar cells based on silicon wafer (1G). In the Thin Film solar cells, the absorber layers are generally polycrystalline films deposited or formed on electrically active or passive substrates, such as soda lime glasses, plastics, ceramics, steel, or metallurgical silicon. Among the most promising materials for second generation there are amorphous-Si (a-Si), polycrystalline-Si (p-Si), CuIn(Ga)Se<sub>2</sub> (CIGS), CdTe/CdS. In particular CIGS and CdTe, show a peculiar direct band gap allowing to absorb the solar radiation much more efficiently than crystalline silicon. This high absorbing efficiency makes using only 1-10 µm thick films as active material possible in solar cell structures. As a result, the main advantage achieved using thin Film Technology is represented by the low manufacturing cost, due to the low cost of both processing and materials. Currently, the efficiency and fabrication cost per unit area are already comparable to those of first generation solar cells. However, the main disadvantages showed by such technology are the long-term instability, due to chemical reaction of the surface absorber layer with O<sub>2</sub> and water vapor, scarce reproducibility technical difficulty in achieving the required uniformity over large areas and, above all, the requirement of a multi-stage fabrication process for photoreactive thin film manufacturing [5-6]. Worldwide research efforts has allowed to obtain solar cells with a record efficiency (n) of 19.4% and 16.7% for CIGS and CdTe based solar cells, respectively [7-8]. Recently, at the ZSW (Zentrum für Sonnenenergie- und Wasserstoff-Forschung ) a CIGS device with active area of 0.5 cm<sup>2</sup> and a record efficiency of 20.3% has been

obtained by thermal-co-evaporation method [9]. Several companies such First Solar, Globalsolar, Nanosolar, Solopower, Honda, etc, have developed and produced modules able to produce several gigawatt per year, employing commercial CIGS based cells with efficiencies of 13.5% [10].

The state of art efficiencies extracted for solar cells based on several crystalline and amorphous photoreactive materials are summarized in Table.1.1.

S.No	Solar cell	η(%)	Ref.
1	CIGS	20.3	[9]
2	CdTe	15.8	[11]
3	CZTS	10	[12]
4	GaAs multijunction	41.1	[13]
5	Si	24.5	[14]
6	Polymer	7	[15]
7	DSSC	11	[16]

Table.1: Highest efficiencies of state of art solar cells based on different materials.

CIGS based solar cells are the most promising in terms of performance in the context of Thin-Film Technology (table 1). The highest performance, combined with the fundamental capability of processing the material by means of a single stage technique, both concur in making CIGS one of the most promising candidates to enhance the renewable resources use for energy production. The importance of materials and device processing is clearly obvious in view of low production cost. In this respect, preparation of CIGS based devices via Pulsed Electron Deposition (PED) allows to avoid the selenization step for the preparation of the active thin layer in solar cells. The study of CIGS based solar cells properties, fabricated using PED technique, plays an important role in view of an all-PED thin films solar cell manufacturing.

#### References

[1] S.M Sze Physics of semiconductor John Wiley & Sons 1981

[2] M.A. Green, Prog. Photovol.: Res. Appl. 9, 123-135 (2001).

[3] www.depts.washington.edu

[4] U.S. National Renewable Energy Laboratory (NREL). www.nrel.gov.

[5] R. Noufi, K. Zweibel, WPEC4, Hawaii (2006).

[6] A.D. Compaan, J.R.Sites, R.W. Birkmire, Electrochemical Society Symposium Proceedings, ECS99-11 (2003).

[7]X. Wu, et al., Proceedings of 17th European Photovoltaic Solar Energy Conference, Munich, 22–26 Oct., 995–1000 (2001).

[8] I. Repins, et al, IEEE Photovoltaics Specialists Conference Record, 33 (2008).

[9]M.Powella, Zentrum fur Sonnenenergie und Wasserstoff-Forschung Baden-Wurttemberg, Germany.www.pv-tech.org,August 29<sup>th</sup> 2010.

[10] T.Cheyney, Photovoltaics international second ed. 2008

[11] J.Britt, C.Ferekides, Appl. Phys. Lett. 62 (1993) 2851.

[12] IBM. Private communication 2010.

[13] F.Dimorth, et al., Fraunhofer Institute for Solar Energy Systems.www.nextbigfuture.com, May 19<sup>th</sup> 2010.

[14] J.Zhao, et al., Appl.Phys Lett.66 (1995) 3636.

[15] H.Y.Chen, et al., Nature 3 (2009) 649.

[16] S.Ito, et al., Thin Solid Films 516 (2008) 4613.

# 1. CIGS based solar cells

### 1.1 CIGS based solar cells architecture.

The basic structure of a Cu(In,Ga)Se2 thin-film solar cell is depicted in Figure 1.1



Figure 1.1: basic structure of a Cu(In,Ga)Se2 thin-film solar cell [1].

The most commonly used substrate is soda-lime glass, 1-3 mm thick, covered by a thin molybdenum film (300 nm-1 $\mu$ m thick) acting as the backside ohmic contact. The Na content in soda-lime has been shown to be useful for enhancing the solar cell performances, as it diffuses through the Mo film and increases open circuit voltage [2], as well as p-type conductivity and average grain size [3]. The heterojunction is constituted by a p-CIGS layer (thickness ranging between 1.5 and 2.5  $\mu$ m) and a transparent conducting oxide (TCO, usually Al-doped ZnO), buffered by a thin layer of CdS (or ZnS, ZnMgO) and a layer of undoped ZnO. As remarked above, CIGS is a p-type semiconductor with a carrier concentration of about 10<sup>16</sup> cm<sup>-3</sup> [4], while Al-doped ZnO is a n-type semiconductor with a carrier concentration of 10<sup>20</sup>cm<sup>-3</sup> [4]. This asymmetric doping causes the space-charge region to extend much more inside the CIGS film than into the ZnO layer. The front contact is generally composed by Al

or alternate nichel (Ni)/Al layers. Finally, an antireflecting coating (100-200 nm thick layer of MgF<sub>2</sub>) aimed at avoiding light losses due to the semiconductor-air interface.



Figure. 1.2: CIGS based solar cell with a Zns buffer layer in place of CdS [5].

The device architecture described above is considered as a benchmark in literature. Of course, different variations have been proposed in order to overcome some operating and technological limitations. In this respect, an alternative structure has been considered and compared to the standard cell in this work thesis too (Figure1.2). In fact, the CdS buffer layer, deposited generally by chemical bath deposition, can be replaced by a zinc sulfide (ZnS) thin layer, deposited by PED. In this way, remarkably, an all-PED process has been employed to fabricate the entire solar cell, thus allowing an in-situ fabrication and the related control of materials quality. In addition, the use of Cd is undesirable for its environmental impact and commercial potential. Moreover, the quantum efficiency of CdS/CIGS solar cells drops at shorter wavelengths due to optical absorption loss occurring in the CdS layer. Conversely, ZnS has a wider energy band gap than CdS, so it can enhance the blue response of

the photovoltaic cells. So far, there are only few works reporting about highefficiency CIGS devices where the CdS buffer layer is replaced by ZnS [6-7].

### **1.2 CIGS material properties.**

Polycrystalline  $Cu(In_xGa_{1-x})Se_2$  (CIGS) is a II-III-VI<sub>2</sub> is a nonstoichiometric compound with intrinsic p-type semiconducting properties. CIGS is composed by four elements: copper, indium, gallium and selenium. CIGS shows a typical [8] chalcopyrite structure deriving from the group IV class of tetrahedrally bonded semiconductors (Figure 1.3), similar to zincblende (ZnS) one, according to the Grimm-Sommerfield rule.

Different compounds can be obtained by varying the stoichiometry in the chemical formula  $Cu(In_xGa_{1-x})Se_2$  from 1 (pure (copper indium selenide, CIS) to 0 (pure copper gallium selenide, CGS).



Figure 1.3: Chalcopyrite CIGS structure.

CIGS has a tetragonal unit cell with a ratio of lattice parameters c/a close to 2, showing thus a tetragonal distortion arising from the different strength of the Cu-Se, In-Se and Ga-Se bonds. The band gap is tunable by varying the gallium stoichiometric value, ranging from 1.04 (CIS) to 1.68 eV (CIG).

The pseudo-binary phase diagram, where  $\alpha$  is the CIS chalcopyrite structure,  $\delta$  is a high-temperature (HT) phase with the sphalerite structure, and  $\beta$  is an ordered defect compounds (ODC) phase, is reported In Figure 1.4.

Interestingly CIGS shows a high tolerance against defects, making it so valuable for photovoltaic applications. This is because of both its tolerance for off-stoichiometric compositions and the electrically neutral nature of its structural defects. Typical average compositions of device-quality films have 22 to 24 at.% Cu, which fall within the single-phase region at growth temperature (500°C).



Figure 1.4: CIGS pseudo-binary phase diagram [4].

Finally, it is worth noting that the chalcopyrite phase field is increased by the addition of Ga or Na [9]. As a result, the Na inclusion in the CuInSe2 structure causes a

replacement of InCu antisite defects by Na atoms, thus reducing the density of compensating donors [10] The calculated effect of Na inclusion is therefore consistent with the increase of compositional range in which single-phase chalcopyrite exists and shows an higher conductivity, as experimentally observed.

The high absorption coefficient ( $\alpha > 10^5 \text{ cm}^{-1}$ ) and the p-type behavior obtained when CIGS is grown in an excess of selenium (with a hole concentration of  $10^{16}$ - $10^{17} \text{ cm}^{-3}$  and a record in charge carrier mobility of 200 cm<sup>2</sup>/Vs), make CIGS films very promising as absorber layers in thin film solar cells, so that conversion efficiencies exceeding 20% were demonstrated in laboratory device prototypes[11].

CIGS morphological features are essentially connected to the growth technique used for thin film deposition. In fact, CIGS thin films show a typical polycrystalline morphology whose physical properties are strongly affected by the presence of grain boundaries. It is reported that morphology is crucially influenced by many factors, such as the bilayer precursor film features, the selenization parameters (e.g. flux during selenization) [12] and the precursor deposition technique [13]. Thus, optimizing CIGS growth procedure may represent a key step to make thin film solar cells competitive in the energy production market.

### **1.3 CIGS growth processes**

For photovoltaic purposes, CIGS film has been deposited onto different substrates such as metalized Soda Lime Glass, steel, ceramic, polyimide. Among the different deposition processes developed for the production of CIGS solar cells, thermal coevaporation [14], sputtering/selenization [15] and electrodeposition [16] have so far emerged as the preferred candidates for industrial scale-up, due to the right compromise given in terms of production cost and performance. However all these techniques still present serious limitations and drawbacks which are causing a delay in the industrial take-off of CIGS solar cells.

#### **1.3.1 Thermal co-evaporation**

In particular, the thermal co-evaporation, which allows high efficiency solar cells to be obtained, is a three stage process carried out in line, under vacuum conditions, involving four precursors (Cu,In,Ga,se), each one being deposited by means of an independent Knudsen cell. The glass substrates move in line over the top of the elemental sources, four in total, with a speed of 1 cm/min (Figure1.5).



Figure. 1.5 Scheme of line co-evaporation process system [17].

During the first step of the process, In-Ga-Se are deposited onto Mo coated soda lime glass at 350°C, thus obtaining (InGa)<sub>2</sub>Se<sub>3</sub> compound, then a second deposition of Cu and Se at 500°C follows. Finally in third stage In,Ga and Se are deposited in order to obtain CIGS films [17]. It is worth noting that multi-stage co-evaporation, that gave 20.3% lab-record efficiency [11], is generally considered to be unsuitable for mass production because of its complexity and poor composition reproducibility in large manufacturing systems.

#### 1.3.2 Sputtering

Sputtering of metal precursors followed by a post-growth selenization step appears to be a more feasible route for industrial scale-up, but the unavoidable selenization stage [18-19] is a major issue in terms of environmental impact (highly toxic  $H_2Se$  is usually used) as well as the operation costs linked to high temperature processing still represent a weak point for such technique [20].

In order to overcome the limitations associated with multi-stage deposition, several single-stage processes based on sputtering and co-evaporation have been proposed as more cost-effective alternatives. Reported efficiencies for lab-scale cells are typically lower than 12.5%, even if in ref [21] a conversion efficiency of 15.9% in the case of a single stage co-evaporation process, carried out at a substrate temperature ( $T_{sub}$ ) of 550 °C, is reported.

High quality thin films can be deposited by means of sputter coating technique. This process typical PVD method discovered in the middle of 19<sup>th</sup> century. At present time, the control of environmental conditions allows to enhance the film quality. The method exploits a gaseous plasma accelerated towards the cathode. In practice, the cathode represents a target constituted by the reference material. Neutral charged atoms can be extracted and collected on a suitable substrate by hitting this target. The plasma is generated using an inert gas (typically Argon) and a magnetron. Collisions between electrons and gas atoms are favored by strong electric and magnetic fields, thus generating the plasma. Sputter source can by supplied by direct current (DC) and alternate current at radiofrequency (RF). RF sputtering systems are used to produce highly insulating oxide films while DC power supply is dedicated to deposit pure metals and, more in general, conductive compounds.

CIGS can be obtained by a two steps process. First, CIG is deposited by co-sputtering copper, indium and gallium at room temperature or near room temperature. The co-sputtering allows obtaining a stacked multilayer metallic structure, characterized by a

high degree of crystallinity and very smooth surfaces. CIGS formation is then favored by an annealing procedure in presence of selenide vapor. The selenization step is performed at high temperature supplying the selenium in a gas phase ( $H_2Se$  or elemental Se). The temperature assisted incorporation of selenium (adsorption and subsequent diffusion in CIG films) occurs in terms of formation of intermediate metal-selenide binary compounds. Unfortunately, a phase separation of different stoichiometric CIGS compounds occurs, due to the complexity of reaction occurring during the selenization process, so the control of such a deposition process is actually difficult [22].

#### **1.3.3 Electro-deposition**

Vacuum technologies are often considered not desirable for the production of a low cost technology. Non vacuum processes are what worldwide researchers pursue in order to reduce costs. Such methods allow to produce good quality CIGS with a low material waste. CIGS produced by non-vacuum methods, when used as absorber layer in PV application, is gave a record conversion efficiency of 13.95% [23]. Among the non-vacuum processes, electrodeposition seems to play a crucial role for the deposition of CIG precursor. In general, electrodeposition of Cu-In-Ga alloys is carried out onto Molibdenum substrates from aqueous solutions containing the precursors (e.g. CuCl, InCl3 and Ga(NO3)3•7H2O). By applying a static potential between a saturated calomel electrode (SCE) and a platinum counter electrode, CIG films can be produced [24]. However, also electro-deposition requires a high temperature selenization process that leads to the drawbacks mentioned above.

#### **1.3.4 PED technique**

Pulsed Electron deposition is a typical ablation (non-equilibrium extraction of the target material) process in which a pulsed (100 ns) high power electron beam (approximately 1000 A, 15 keV) penetrates approximately 1  $\mu$ m into the target, thus provoking a rapid evaporation of target material and subsequent formation of a plasma state. In detail, the electron flux extracted by the plasma passes through a hole and then is driven towards the target by means of an alumina tube with a diameter of few mm. The high potential difference applied between the cathode and the target holder accelerates this flux.

In this way, very high current density in the beam (about  $10^6$  A/cm<sup>2</sup>) and subsequently very high power density (up to  $10^9$  W/cm<sup>2</sup>) are obtained. The ablation facilitates stoichiometric composition of the plasma, thus preserving the target stoichiometry in the deposited films.

The cathode, operating in pulsed mode, is made by a metal tube in which electrons are generated via ion impact or photo effect. The electron flux is driven towards a narrow exit and controlled by a trigger circuit, avoiding thus discharge voltage [4]. The acceleration system designed for PED allows obtaining an intense pulsed electron beam. A fast evaporation of the material target hit by the high power density beam and the subsequent formation of a plume composed by ablated material occur. The penetration depth of the electron beam inside the target is about 1  $\mu$ m, due to the energy losses provoked by scattering and Coulomb interactions. Nevertheless this penetration length is ten times greater than absorption length of laser radiation, resulting in a deposition rate for PED at least ten times greater than that obtained by Pulsed Laser deposition technique.

As regarding the plume properties, keeping in mind that it expands in the maximum pressure direction, generally some theoretical models are able to predict the optimized distance between substrate and target in order to obtain uniform films over wide surfaces (5-6 cm) with a good control. At present time, the basic phenomena and the physics of the discharge are not completely understood. Some studies have shown that the generation of particulates interfere with optimal film growth. Nevertheless, The influence of ambient pressure and accelerating potential on the number and size of particulates appearing on the surface of films can be controlled acting on the ambient pressure and accelerating voltage, thus reducing the size of particulates below 100 nm [4]. So the control of deposition parameters allows to manufacture good quality films with controlled defects. Moreover, the possibility to control the formation of particulates could make PED useful for generating submicron sized materials.

The scheme of the PED system installed at IMEM laboratory in Parma is shown in fig. 1.6. The system is composed by a vacuum chamber equipped with an electron source (pulses of 100 ns and power density of  $10^8 \text{ W/cm}^2$ ) and a water-cooled Pfiffer turbo-molecular pump (1200 l/s), an heater based on IR-lamps properly designed to keep a uniform 700°C temperature along 60 cm used for the annealing in reduced atmosphere, being the annealing aimed to remove contaminants (oxide), a glass tube with inner diameter of 2-4 mm for focusing the electron beam, a target holder made of copper (the angle between the electron beam and the holder is 45° in order to optimize the impact onto the target with the minimum shadowing effect), a trigger circuit for frequency regulation and the gas-flow control system to provide the necessary amount of gas to ignite the plasma in the hollow cathode.



Fig 1.6 PED scheme of the system installed at the IMEM-Cnr laboratory

The system is suitable for the deposition of CIGS films with [112]-oriented grains at low growth temperatures ( $250^{\circ} \div 300^{\circ}$ C), using a stoichiometric quaternary target. Also the substrate temperature is lower compared to those required by sputtering and co-evaporation techniques The system clearly allows to obtain an efficient single stage process which is highly desirable for low cost production purposes.

As a matter of fact, PED is a versatile technique for the fabrication of solid state materials-metals, semiconductors and insulators.

### References

[1] www.energy-daily.com/reports/Global\_Solar\_Energy.

[2] J. Hedstrom et al., Swedish Inst. of Microelectron. DOI:10.1109/PVSC.1993.347154 In proceeding of: Photovoltaic Specialists Conference, 1993., Conference Record of the Twenty Third IEEE.

[3] Advanced Materials 10: 31–36

[4] F.Pattini Growth of oxide thin films for energy devices by Pulsed Electron Deposition 2009.

[5] S.Rampino et al., Appl.Phys.Lett 101, 1332107 (2012).

[6] C. Platzer-Björkman et al., J. Appl. Phys. 100, 044506 (2006).

[7] A. Ennaoui, et al., Sol. Energy Mater. Sol. Cells 67,31 (2001).

[8] M. Chandramohan et al., Band structure calculations of Cu(In1-xGax)Se2 Materials Science and Engineering: B Volume 174, Issues 1–3, 25 October 2010, Pages 200–204

[9] R. Herberholz, et al., Eur. Phys. Journal AP (1999) 6.

[10] S.Wei, et al, J. Appl. Phys. (1999) 85.

[11] M.Powella, Zentrum fur Sonnenenergie und Wasserstoff-Forschung Baden-Wurttemberg, Germany.www.pv-tech.org,August 29<sup>th</sup> 2010.

[12] Thin solid films Volumes 431–432, May 1<sup>st</sup> 2003, Pages 31–36.

[13] Thin solid films Volume 474, Issues 1–2, 1 March 2005, Pages 10–13.

[14] I. Repins, et al., Prog. Photovolt: Res. Appl. 16, 235 (2008).

[15] R. Caballero, et al., Prog. Photovolt.: Res. Appl. 14, 145 (2006).

[16] M. Ganchev, et al., Thin Solid Films 511–512, 325 (2006).

[17] T.Negami et al., Sol.Energy Mater.Sol Cells 67 (2001) 1.

[18] M. Marudachalam, et al., Appl. Phys. Lett. 67, 3978 (1995).

[19] A. Bosio, et al., Cryst. Res. Technol. 46, 857 (2011),

[20] S.R. Dhage, et al., J. Electron. Mater. 40, 122 (2011)

[21] W. N. Shafarman, and Jie Zhu, Thin Solid Films 361-362, 473 (2000)

[22] B. J. Stanbery (2002). Critical Reviews in Solid State and Materials Science 27: 73.

[23] J.K:J. van Duren et al., Mater. Res.Soc.Symp. Proc 1012 (2007), (1012-Y05-03).

[24] Thin Solid Films vol 511-512 325-327.

# The physics of solar cells

## 2.1 Solar radiation spectrum.

The radiative energy output from sun derives from nuclear reaction into its nucleus. At second time scale, about  $6x10^{11}$  Kg of hydrogen are turned to helium, with a net mass loss of about  $4x10^3$  Kg, which is converted according the Einstein's relation (E=mc<sup>2</sup>) to  $4x10^{20}$  J.



Figure 2.1: Worldwide distribution solar energy [1].

The amount of energy reaching the surface of the Earth every hour is greater than the amount of energy used by the Earth's population over an entire year. Incident solar radiation on Earth's atmosphere is quite constant, but radiation on Earth's surface varies (Figure 2.1). This variation depends on: latitude of the locations, season, and time; local variations in the atmosphere (for example pollution or clouds) and atmospheric effects like absorption and scattering. All these elements concur to create variations in the overall incident power, in the spectral content of the light incident on Earth, if compared to its content in atmosphere, and in the angle of light incident on the surface. These variations of solar radiation sometimes are too much pronounced.

Desert regions tend to have lower variations due to the lack of local atmospheric phenomena such as clouds. Equatorial regions have low variability between seasons.

#### 2.1.1 Air Mass

Air Mass is defined as the actual path length of light through the atmosphere normalized to the shortest possible path length (that is, when the sun is directly overhead). Air Mass quantifies the reduction in the power of light as it passes through the atmosphere and is absorbed by air and dust. Air Mass is defined as:  $AM=1/\cos\theta$ , where  $\theta$  is the angle formed by light compared to the vertical (zenith angle). Air Mass is 1 if the sun propagates vertically in the atmosphere . Two parameters in solar cells efficiency (power and spectrum of incident light) vary in function of Air Mass coefficient. For this reason, a standard spectrum with a well-defined power density has been introduced with the aim of having uniformity in experimental results concerning solar cells measures (at different time and locations). We define the standard spectrum at the Earth's surface as AM1.5G, (the G stands for global and includes both direct and diffuse radiation) or AM1.5D (which includes direct radiation only).

AM1.5D intensity radiation can be approximated by reducing the AM0 spectrum, which is equivalent to the spectrum emitted by a 6500 K black body (1353 W/m<sup>2</sup>), by the absorption and scattering contributes of atmosphere: AM1.5D is then equal to 768 W/m<sup>2</sup> and AM1.5G to 970 W/m<sup>2</sup> (Figure 2.2 ) [2].However, the standard AM1.5G spectrum has been normalized to 1 kW/m2, due to the convenience of the round number and the fact that there are inherently variations in incident solar radiation.



Figure 2.2: Comparison between the spectra of a 6500K black body (green) and the solar radiation outside the Earth's atmosphere (red) and on the Earth's surface (blue) [2].

### 2.2 Introduction to the Basic principles of solar cells.

Solar cells convert solar energy into electricity, in a more or less efficient way. Active materials suitable for this purpose are semiconductors in their basic structure based on p-n junction. The solar cell in its current design has been developed by Chaplin, Fuller and Pearson [3] in 1954, using a diffused silicon p-n junction. Subsequently, solar cells based on cadium-sulfide have been developed be Raynold [4]. Over the years, solar cells have been made using other semiconductors (Germanium, III-V, II-VI), recurring to different material and device configurations such as single crystals, polycrystalline or amorphous materials, organics deposited in the form of thin films, forming homojunctions or heterojunctions.

A simple and conventional solar cell structure is showed in Figure 2.3 in detail, the cell consists of:

- a) active absorber layer made of a semiconductor material, generally with a ptype charge transport;
- b) buffer layer generally made by a n-type semiconductor;

- c) anti-reflecting coating layer(AR);
- d) back and front metallic contacts for collect the generated electrons and holes



Figure 2.3: Schematic solar cells structure [5].

The absorption of solar radiation in solar cells is characterized by a threshold photon energy  $\hbar\omega_g$ . The photons with energy higher than  $\hbar\omega_g$  can be absorbed, while the photons with lower energy are either reflected or transmitted. Incident photons with appropriate energy (higher than energy gap of semiconductor materials) are absorbed, favoring the promotion of a neutral excitation, called exciton, constituted by electronhole pairs. Current generation is obtained upon the exciton dissociation induced by the internal electric field present at the junction, which on its turn drifts the free electrons and holes towards the n- and p-material respectively (Figure 2.4).

An electrical current, called  $I_{sc}$  (i.e. short circuit current) is generated when the charge carriers reach the contacts at the extremity of the p-n junction before recombining.

At the same time, the charge separation creates a voltage between the electrodes of the solar cell. Such voltage, under open circuit conditions, is named " open-circuit voltage" ( $V_{oc}$ ).



Fig 2.4: schematic band structure of p-n junction solar cell [6].

### 2.3 Basic operation principles

#### **2.3.1 Ideal I-V characteristic**

The solar cells is assumed to have ideal I-V characteristics. The equivalent circuit is shown in (Figure 2.5). By the electrical point of view the solar cell is equivalent to a current generator in parallel with a diode. When illuminated, it produces a photocurrent proportional to the light intensity. That photocurrent is divided between the variable resistance of the diode and the load with a proportion depending on the optical power level of incident light and the value of the load resistance. For high load resistances, the photocurrent tends to flow mainly through the diode, resulting in a higher voltage drop between the cell terminals and a smaller current flowing through the load. The diode thus provides the photovoltage [7].



Figure 2.5: Equivalent circuit of ideal solar cell.

In (Figure 2.6) is shown the typical J-V curve of the solar cell in the dark (green line) and the light-generated current (red line).



Figure 2.6: Ideal J-V curves for a solar cell in the dark (green) and during the illumination (red) indicating the short-circuit current  $J_{SC}$  and the open-circuit voltage  $V_{OC}$ .

The J-V curve can shift towards negative current density values due to the effect of light. By illuminating the cell, a light generated current  $I_L$  is subtracted to the dark current flowing into the diode (I <sub>DIODE</sub>), so that the total current flowing between the device terminals, I, becomes:

$$I = I_0 \left( exp \frac{qV}{nK_b T} - 1 \right) - i_L = I_{diade} - I_L \quad (2.1)$$

where q is the is the elementary electron charge, n is the diode ideality factor (n=1 in the ideal case,  $1 < n \le 2$  in presence of generation-recombination centers), T is the absolute temperature and K<sub>b</sub> the Boltzmann constant. The dark saturation current I<sub>0</sub> is given by:

$$I_0 = \left(\frac{qD_n n_i^2}{L_n N_A} + \frac{qD_p n_i^2}{L_p N_D}\right) \quad (2.2),$$

where  $D_n (D_p)$  is the electron (hole) diffusion constant,  $n_i$  the intrinsic concentration of the material,  $L_n (L_p)$  the electron (hole) diffusion length in the p- (n-) region,  $N_A$  $(N_D)$  the net acceptor (donor) concentration in the p- (n-) region. The presence of the  $-I_L$  in eq. 2.1 indicates that the I-V characteristic is shifted so that in both 1<sup>st</sup> and 3<sup>rd</sup> quadrants the product VI is positive, thus indicating power consumption, while in the 4<sup>th</sup> quadrant VI is negative, which indicates that power can be delivered from the junction to a load. From I-V curves it's possible to extract the three main parameters characterizing this power generation: the short-circuit current (I<sub>SC</sub>), the open-circuit voltage (V<sub>OC</sub>) and the fill factor (FF).

#### 2.3.2 Short-circuit current

We define Isc as the current flowing through the solar cell when the junction is short circuited, i.e. the voltage across it is zero. It is worth noting that the short circuit current corresponds to the light-generated current for an ideal solar cell (which is engendered by the generation and collection of light-generated carriers) in the case of very moderate resistive loss mechanisms.

The short-circuit current is influenced by several factors, such as:

- the illuminated solar cell area;

- the power of the incident light (i.e. density of photons per unit time);

- the incident light spectrum, usually standardized to the AM1.5 spectrum;

- optical properties, i.e. absorption of the active material and reflections at the solar cell interfaces;

- the collection probability of the solar cell, expressed as a normalized factor, depending essentially on the passivation of surface and the minority carrier lifetime. Collection probability describes the probability that a light generated carrier, absorbed in a certain region of the device, is collected by the p-n junction and therefore contributes to the light-generated current. Such probability depends on the distance between the p-n junction and the charge generation center compared to the diffusion length, that is the average distance over which a recombination of holeelectron pairs occurs. Collection probability also depends on the surface properties of the device. The collection probability of carriers generated in the depletion region is 1, as the electron-hole pair are quickly swept apart by the electric field and are collected. The collection probability drops as the distance between the generation center and the junction increases. If the carrier is generated at a distance from the junction which is larger than the diffusion length, then the collection probability of this carrier approaches to zero. Similarly, if the carrier generation occurs closer to an interfacial region where the recombination rate is high, then the carrier will recombine in that region, thus reducing the collection probability. An overall picture of the above mentioned collection probability features is given in Fig.2.7.



Figure 2.7: collection probability behavior as a function of distance in device. The maximum collection probability is found into the depletion region [2].

The collection probability in conjunction with the generation rate in the solar cell both determine the light-generated solar cell current. The equation for the lightgenerated current density  $(J_L)$ , with an arbitrary generation rate (G(x)) and a collection probability (CP(x)), is given by:

$$J_{L} = q \int_{0}^{W} G(x) CP(x) dx = q \int_{0}^{W} \left[ \int \alpha(\lambda) H_{0} \exp(-\alpha(\lambda)x) d\lambda \right] CP(x) dx \quad (2.3),$$

where:

q is the electronic charge;

W is the thickness of the device;

 $\alpha(\lambda)$  is the absorption coefficient;

 $H_0$  is the number of photons at each wavelength.

It is clear that a non-uniform collection probability will cause a spectral dependence in the light-generated current.

#### 2.3.3 Open-circuit voltage

The open circuit voltage, denoted as  $V_{oc}$ , is the voltage for J=0, that is the maximum voltage available from a solar cell under illumination. If the reverse saturation current  $I_0$  increases, then the  $V_{oc}$  value decreases. An expression for  $V_{OC}$  is obtained from the equation (2.3) by setting J=0:

$$V_{oc} = \frac{nK_bT}{q} \ln \begin{pmatrix} I_L \\ I_O \end{pmatrix} + 1$$
(2.4)

The  $V_{OC}$  depends on the ratio between the saturation current  $I_0$  of the solar cell and the light-generated current  $I_L$ . In this respect,  $I_0$  experiences strong variations due to its dependence on the  $n_i^2$  factor, being able to increase by many orders of magnitude and it is also influenced by recombination in the solar cell (see equation 2.2), while  $I_L$ shows only small variation. So the variations in  $V_{OC}$  are strictly connected to the material properties.

It possible to define the  $V_{OC}$  in an alternative way from the carrier concentration, as described in ref. [8], obtaining the so called "Implied  $V_{OC}$ ":

$$V_{oc} = \frac{K_B T}{q} \ln \left[ \frac{(N_A + \Delta n) \Delta n}{n_i^2} \right] \quad (2.5)$$

where  $k_BT/q$  is the thermal voltage and  $\Delta n$  is the excess carrier concentration. Finally, it is worth noting that while the short-circuit current decreases with increasing band gap, the open-circuit voltage increases as the band gap increases.

### 2.3.4 Fill factor

The "Fill Factor", defined as the ratio between the maximum power delivered by the cell and the product of  $J_{sc}$  and  $V_{OC}$ , is given by:

$$FF = \frac{I_{mV_m}}{I_{sc}V_{oc}} \quad (2.6)$$

where  $J_m$  and  $V_m$  are the current and voltage maximizing the power generated by the cell, whose product defines the maximum power ( $P_{max}$ ) (Fig.2.8).



Figure 2.8: Cell output current (red line) and power (blue line)as function of voltage. The cell short-circuit current (ISC)and open-circuit voltage (VOC) points, as well as the maximum power point (Vmp, Imp) are shown too. The fill factor (FF) is given by the ratio between the large light rectangle (VOC×ISC) and the smaller dark one [2].
Graphically, the FF is a measure of the "squareness" of the I-V characteristic (Figure 2.8). The FF is one of the parameters chosen for 'calibrating' the stability of solar cells. The maximum theoretical FF from a solar cell can be obtained from the derivative of the power generated by a solar cell with respect to the voltage. Moreover, the FF has been empirically determined as follows [9]:

$$FF = \frac{V_{oc} - \ln (V_{oc} + 0.72)}{V_{oc} + 1} \quad (2.7)$$

The above expression shows that a higher FF corresponds to a higher voltage. However, large variations in open-circuit voltage are relatively uncommon for different materials, while the variation in maximum FF can be significant for solar cells based on different semiconductors.

#### 2.3.5 Efficiency

The efficiency is the most commonly used parameter to express the performance of a solar cell. Efficiency is defined as the ratio of energy output of the solar cell to the input energy from the sun, that is determined as the fraction of incident power which is converted to electricity. Efficiency depends on the spectrum and intensity of the incident sunlight and the temperature of the solar cell.

It has to be kept in mind that terrestrial solar cells are measured under AM1.5 conditions (more specifically under AM1.5G spectrum) at a temperature of 25° C. Solar cells intended for space use are measured under AM0 spectrum.

The expression of the efficiency of a solar cell is defined as:

$$\eta = \frac{P_{max}}{P_{in}} = \frac{V_{oclss}FF}{P_{in}} \quad (2.8)$$

In terms of conversion efficiency, there are two competing effects regarding the enhancement of solar cell performance. On one hand, in fact, the lower the band gap is, the more low energy photons the cell will absorb; as a result  $J_{SC}$  will rise. However, low band gap diodes will have a large dark current due to the  $n_i^2$  dependence of the reverse saturation current, as shown by equation (2.2). So the optimization of the band gap is required due to the competition between these phenomena.

### 2.3.6 Characteristics resistance.

The characteristic resistance  $(R_{ch})$  of solar cells is shown in Figure 2.9.



Figure 2.9: Characteristic resistance of a solar cell [2].

It is defined as the output resistance of the solar cell at its maximum power point. If the resistance of the load is equal to the characteristic resistance of the solar cell, then the maximum power is transferred to the load and the solar cell operates at its maximum power point. It is a useful parameter in solar cell analysis, particularly when examining the impact of parasitic loss mechanisms.

 $R_{ch}$  can be approximately expressed as the ratio between  $V_{OC}$  and  $I_{SC}$ :

$$R_{ch} = \frac{V_{nc}}{I_{sc}} \quad (2.9)$$

#### 2.3.7 Effect of parasitic resistances.

In real devices, resistive effects reduce the efficiency of the solar cell due to power dissipation in the parasitic resistances. The most common parasitic resistances are the series resistance ( $R_s$ ) and the shunt resistance ( $R_{sh}$ ) as shown in Figure 2.10.



Figure 2.10: Parasitic series and shunt resistances in a solar cell circuit [2].

If parasitic resistances are included, the diode equation (2.1) becomes:

$$I = I_{diode} + I_{sh} - I_L = I_0 \left[ \frac{q(V-R_s)}{nR_BT} - 1 \right] + \frac{V - IR_s}{Rsh} - I_L \quad (2.10)$$

Series and shunt resistance depend on the geometry of the solar cell, at the operating point of the solar cell. Since the value of resistance will depend on the area of the solar cell, when comparing the series resistance of solar cells with different areas, it is useful to express it as an area-normalized resistance (expressed in  $\Omega \text{cm}^2$ ). This area-normalized resistance can be extracted by replacing the current with current density in Ohm's law, as shown below:

$$R'(\Omega cm^2 = \frac{V}{J} \quad (2.11)$$

Series resistance in a solar cell arise from three phenomena:

• the movement of current through the solar cell;

- the contact resistance between the metal contact and the active semiconducting materials
- the resistance of the top and rear metal contacts.

The main impact of series resistance is to reduce the fill factor, although excessively high values may also reduce the short-circuit current. Significant power losses caused by the presence of a shunt resistance,  $R_{sh}$ , are typically due to manufacturing defects, rather than poor solar cell design. Low shunt resistance causes power losses in solar cells by providing an alternative current path for the light-generated current. Such a diversion reduces the amount of current flowing through the solar cell junction, thus reducing the voltage across the solar cell (Figure 2.11 a). The effect of a shunt resistance is particularly severe at low light levels, since there will be less light-generated current. Therefore, the loss of current occurred due to the shunt resistance has a larger impact in respect to  $R_s$ . In addition, at lower voltages, where the effective resistance of the solar cell is high, the impact of a resistance in parallel is large. The effect of  $R_{sh}$  on the I-V curve is shown in (Figure 2.11 b). An estimation of the shunt resistance value of a solar cell can be carried out from the slope of the I-V curve near the short-circuit current point.



Figure 2.11: Effects of (a) increasing series resistance and (b) reducing parallel resistance on the light I-V characteristics of solar cells.

#### 2.3.8 Effect of temperature.

As it happens for all semiconductor based devices, solar cells are sensitive to the environmental temperature. An increase of temperature reduces the band gap of a semiconductor, thus affecting most of the semiconductor material parameters. The decrease in the band gap of a semiconductor with increasing temperature can be viewed as an increase of the electrons energy in the material. In a solar cell, the parameter most affected by an increase in temperature is the open-circuit voltage. The impact of increasing temperature is shown in the figure below (Figure 2.12).



Figure 2.12: Effect of temperature on the IV characteristics of a solar cell [2].

The open-circuit voltage decreases with temperature because of the temperature dependence of  $I_0$ . The equation for  $I_0$  from one side of a p-n junction is given by:

$$I_0 = qA \frac{Dn_l^p}{LND} \qquad (2.12)$$

where q is the electronic charge, D is the diffusivity of the minority carrier, L is the diffusion length of the minority carrier,  $N_D$  is the doping density and  $n_i$  is the intrinsic carrier concentration.

In (2.12) many of the parameters have some temperature dependence, but the most significant effect is due to the intrinsic carrier concentration,  $n_i$ . The intrinsic carrier concentration depends on the band gap energy. The expression for the intrinsic carrier concentration is given by:

$$n_{i}^{2} = 4 \left(\frac{2\pi KT}{h^{2}}\right)^{3} \left(m_{\pi}^{*} m_{h}^{*}\right)^{3/2} \exp\left(-\frac{E_{g0}}{KT}\right) = BT^{3} \exp\left(-\frac{E_{g0}}{KT}\right) \quad (2.13)$$

where T is the temperature, h and k are Plank's and Boltzmann's constants, me and mh are the effective masses of electrons and holes, respectively,  $E_{g0}$  is the band gap linearly extrapolated to absolute zero and B is a constant which is essentially independent of temperature.

Substituting these equations back into the expression for  $I_0$ , and assuming that the temperature dependencies of the other parameters can be neglected,  $n_i$  is given by:

$$n_{i}^{2} = 4 \left(\frac{2\pi KT}{h^{2}}\right)^{3} \left(m_{\pi}^{*} m_{h}^{*}\right)^{3/2} \exp\left(-\frac{E_{g0}}{KT}\right) = BT^{3} \exp\left(-\frac{E_{g0}}{KT}\right) \quad (2.14)$$

where B' is a temperature independent constant. The large variation of  $I_0$  can be understood if one thinks that for silicon solar cells near room temperature,  $I_0$ approximately doubles if temperature increases by 10 °C.

The impact of  $I_0$  on the open-circuit voltage can be calculated by substituting the equation for  $I_0$  into the equation for Voc as shown below:

$$V_{oc} = \frac{KT}{q} \ln\left(\frac{l_{sc}}{I_0}\right) = \frac{KT}{q} \left[\ln I_{sc} - \ln I_0\right] = = \frac{KT}{q} \left(\ln I_{sc} - \ln B' - \gamma \ln T + \frac{qV_{g0}}{KT}\right) \quad (2.15)$$

where  $E_{G0} = qV_{G0}$ . Assuming that dVoc/dT does not depend on dIsc/dT, dVoc/dT can be found as:

$$\frac{dV_{oc}}{dT} = \frac{V_{oc} - V_{g0}}{T} - \gamma \frac{k}{q} \qquad (2.16)$$

#### 2.3.9 Ideality factor

The ideality factor of a diode is a measure of how closely the diode follows the ideal diode equation. In practice, there are second order effects so that the diode does not follow the simple diode equation and the ideality factor provides a way of describing them. The ideal diode equation assumes that all the recombination occurs via band to band or recombination via traps in the bulk of the device, that is out of the junction depletion region. Using that assumption the ideal diode equation is expressed in eq.(2.17) by n=1:

$$I = I_0 \begin{pmatrix} exp & qV \\ nK_bT & 1 \end{pmatrix} \quad I_L \quad (2.17)$$

However recombination occurs in a different way in the case of solar cells. These recombination phenomena produce an ideality factors deviating from the ideal one. From the ideal diode equation it is possible to find the ideality factors corresponding to a particular recombination phenomenon, as indicated in Table II.1.

Recombination Type	Ideality factor	Description
SRH, band to band (low level injection)	1	Recombination limited by minority carrier.
SRH, band to band (high	2	Recombination limited by both
level injection)		carrier types.
Auger	2/3	Two majority and one minority
		carriers required for recombination.
Depletion region (junction)	2	two carriers limit recombination

Table 2.1: Recombination type of solar cells

### 2.4 CIGS Thin Film Solar Cells

CIGS based thin film solar cells show highest efficiency in such a class of solar cells because of several aspects, both regarding the physical properties and the technological impact. In detail, the possibility of varying the band gap between 1.04 eV and 1.68 eV, obtained by varying the Ga composition, allows obtaining the opportune band gap for enhancing the absorption of most of the photons in the solar spectrum; then, the thermal expansion coefficient of CIGS well matches that one of SLG; furthermore, the carrier concentration in CIGS can be varied by controlling its composition, without recurring to extrinsic doping processes, favoring thus the arising of an abrupt junction between CIGS and the window layer; finally, the direct band gap allows the manufacturing of very thin absorber layers, typically 1.2-2,5  $\mu$ m, that is 100 times thinner than Si based solar cells.

The first point is of paramount importance, as the efficiency of cells depends on Ga content. In principle an optical band gap of about 1.55 eV would be desirable, even if it has been demonstrated that record efficiency can be found for lower band gap CIGS based cells. In particular, for gallium concentration beyond x~0.26, corresponding to a band gap of 1.22 eV, then the efficiency decreases because of an increase of defects density due to Ga inclusions.

The prototype record showing the record efficiency(19.5-20.3%) is made of a series of layers, listed starting from the substrate to the antireflective layer, as depicted in Fig.2.12: SLG/Mo/CIGS (2.5-2.75  $\mu$ m)/CdS (50-60 nm)/i-ZnO(90nm)/ZnO:Al (120nm)/Ni-Al/MgF<sub>2</sub>(120nm). The film composition contains 0.8≤Cu/(In+Ga)≤0.95, x~0.3 and band gap of 1.21-1.14 eV. The large grain size showed by CIGS favors the enhancement of efficiency, while smaller grains reduce it up to about 15% [10].



Fig.2.13: scheme of a high efficiency prototypal CIGC thin film solar cell.

It has been demonstrated that CIGS based cells with a low ideality factor and saturation current  $I_0$  exhibit higher efficiency [11-12]. Moreover, typical values for Rs and Rsh are 0.2-0.3  $\Omega$ •cm<sup>2</sup> and 10 K $\Omega$ •cm<sup>2</sup>, respectively [11-12]. Large area prototypes show that CIGS based cells exhibit a lower efficiency (13%) in the case of about 50 cm<sup>2</sup> sized cells [13].

In view of the development of prototypes conceived for implementing the building integration, further study on large area devices, fabricated in particular using nonconventional substrates such as ceramics and cement, are required.

## References

- [1] www.metafilter.com
- [2] C. Honsberg and S. Bowden (http://www.pveducation.org/pvcdrom).
- [3] D.M Chapin et al, J.Appl.Phys., 25, 676 (1954).
- [4] D.C. Raynolds et al., "Photovoltaic Effect in Cadmuim Sulfide" Phys. Rev., 96, 533 (1954).
- [5] http://kids.britannica.com
- [6] www.large.stanford.edu.
- [7] J. Nelson, The physics of solar cells, London, Imperial College Press, 2003.
- [8] R. Sinton et Al., Appl. Phys. Lett. 69, 2510-12 (1996).
- [9] M.A. Green, Solar Cells 7, 337-340 (1982).
- [10] S.Rampino et al., Appl.Phys.Lett 101, 1332107 (2012).
- [11] J. Poortma et al., Thin solid films 480-481 499 (2005).
- [12] M.A. Contreras et al., Prog.Photovolt:Res.Appl, 13 (2005) 209.
- [13] M.A Contreras et al., Prog. Photovolt. Res appl 7 (1999) 311.

# **3** Experimental techniques

# **3.1. Introduction**

The experimental section is devoted to the introduction of all experimental techniques regarding the steps that have been directly developed in this work thesis.

In detail, in section 3.2, Sputter Coating Technique employed for the back contact (molybdenum) deposition, will be introduced. Photolithography, used for the manufacturing of shadow masks (deposition of front contact) or for defining the contact area, will be treated in Section 3.3. Section 3.4 will treat briefly the cleaning procedure adopted for the control of substrate (SLG) properties and cleanliness, that is Hydrogen Plasma Etching. The electrical characterization for the analysis of device performance and properties, consisting in current-voltage (I-V) and capacitance-voltage (C-V) measurements, will be discussed in section 3.5. Section 3.6 will be focused on thermographic analysis of solar cells, aimed to display the presence of shunts, that is detrimental factors in terms of device performance. Then, section 3.7 will treat briefly the technique employed for the film thickness measurements, performed by means of a mechanical profilometer.

Finally, it is worth noting that no reference to cell fabrication on these substrates because the surface quality achieved was not completely compatible with thin film solar cell deposition.

# 3.2 Sputtering technique.

DC sputtering has been used for the molybdenum back contact deposition. Sputtering is a thin films growth technique which allows both metallic (DC and magnetron sputtering) and insulating (RF sputtering) materials to be deposited. This technique is a vacuum process consisting in the transport of the material to be deposited (metal or

insulating) from a source, called target, to a substrate (soda lime glass, ceramic, cement, steel, semiconductor substrates) [1].

The apparatus used here is a DC system where vacuum is provided by a diffusive pump that allows a background pressure of  $10^{-6}$  mbar to be reached [2].

An inert gas is then introduced into the chamber, (generally Ar which has an atomic mass comparable with that one of common metals), to achieve a pressure value between  $10^{-1}$  mbar and  $10^{-4}$  mbar. The inert gas is ionized by applying a voltage between the target (cathode) and sample holder (anode), so that the free electrons in the chamber are accelerated. As a result, the reaction  $Ar + e^- \rightarrow Ar^+ + e^- + e^-$  takes place, producing positive ions  $Ar^+$ . The second electrons produced upon Ag ionization contribute to repeat the above process, until a gas breakdown occurs and a discharge glow, that is a plasma, is produced. Second electrons play another important role in sustaining the formed plasma, in contrast with the voltage drop between cathode and anode followed by the discharge process. Typically, discharge glows are produced for voltages of about 1KV in presence of gases at low pressure.

The target surface is then bombed with positive ions created and accelerated by the potential difference itself (Figure 3.1 a). In this way. The collisions between ions and the target cause an increase of atomic thermal energy amplifying the oscillatory motion inside the crystal lattice.

When the kinetic energy ( $E_c$ ) of Ar ions is greater than the energy bond ( $E_b$ ) of atoms in the crystal lattice, these ones are expelled from target (Figure3.1 b). The energy of the expelled atoms is included between 1 eV and 10 eV and is greater than that obtained by evaporation methods (where in order to obtain the same kinetic energy values it's necessary to operate at temperature greater to  $10^4 \, {}^{\circ}C$ ). In this way, films with a better adhesion on the substrate are deposited [2].



Fig.3.1: a) Schematic sputtering vacuum deposition system b) Sputtering from a linear collision cascade [3].

In order to make the process efficient, a compromise between the electrodes spacing (L) and the Ar pressure is required. In fact, if L is the anode-cathode spacing and P is the gas pressure inside the chamber, the condition required to sustain the plasma is :

$$L*P>0.5$$
 (cm\*Torr) (3.1)

where P is expressed in Torr. Also the deposition rate R depends on gas pressure, but this time a high chamber pressure imply a low deposition rate, as qualitatively R can be expressed as [4]

In particular, the mean free path of atoms  $\lambda$  at a pressure P is generally expressed as:

$$\lambda \sim 5*10^{-3}/P(Torr)$$
 (3.3),

so the condition for sustaining the plasma, considering an electrode spacing of some centimetres, generally corresponds to a mean free path causing hundreds collisions before reaching the target, resulting thus in a reduced deposition rate. All these features imply that the choice of this technique allows a thin film deposition only at low deposition rates. Other techniques such as magnetron sputtering , if required, allow to deposit films at higher deposition rate.

# **3.3 Photolithography**

Photolithography, generally named optical lithography or UV lithography, is a technologic process adopted to transfer some pattern on the surface of a semiconductor. In particular, photolithography exploits light in order to transfer a geometric shape drawn on a mask to a thin layer made of a light-sensitive material (photoresist, PR, or simply resist) covering the surface of a substrate or the surface of a semiconductor upon some chemical treatments. The pattern in the etching resist is created by exposing it to light, both using a mask projecting the image on the resist or directly. Subsequent etching procedures allow obtaining the desired shape on the surface [5].

Photolithography is extremely important due to its very high resolution suitable to create very small sized patterns, up to tens of nanometers (that is below micrometric scale), with a precise control over both shape and size [5].

As far as the PR is concerned, generally this material is a light sensitive liquid used to form thin film. There are several types of PRs. The main property of a PR is that it changes chemically when exposed to a high energy light source. The chemical reaction taking pace on its surface is different in various resists, but generally, all resists become either more (positive resist) or less (negative resist) acidic.

For positive resists, the resist is exposed with UV light wherever the underlying material is to be removed. In these resists, exposure to the UV light changes the chemical structure of the resist, rendering it more acidic, so that it becomes more soluble in the developer (in principle alkali solutions). The exposed resist is then washed away by the developer solution, leaving windows of the bare underlying material. Negative resists behave in just the opposite manner. Exposure to the UV light causes the negative resist to become polymerized, and more difficult to dissolve. Therefore, the negative resist remains on the surface wherever it is exposed, and the developer solution removes only the unexposed portions. Masks used for negative

photoresists, therefore, contain the inverse (or photographic "negative") of the pattern to be transferred. In this work thesis, a popular positive PR, S-1813 (Microposit), has been used.

The steps involved in the photolithographic process are wafer cleaning, photoresist application, soft baking, mask alignment, exposure and development, and finally hard-baking.

In the first step, the wafers are chemically cleaned to remove particulate matter on the surface as well as any traces of organic, ionic, and metallic impurities (the cleaning procedure will be described in the next section).

After cleaning, the PR is deposited on the substrate using spin coating technique.

The Spin coating produces a constant thickness of PR,  $T_{PR}$ , across the sample. The thickness of the PR is inversely proportional to the square root of the spin coater speed (expressed in RPM) [6]:

 $T_{PR} \sim 1/\sqrt{RPM}$  (3.4)

Since the total energy needed for exposure is dependent of the thickness of the film, for high resolution a thin and smooth film is necessary.

After PR deposition, soft-baking makes the PR sensitive to UV light by removing the solvent component of the PR. Because the solvent is now mostly removed, the thickness of the PR is usually decreased by about 25 % [6]. A short prebake will prevent UV light from reaching the photo active component of the PR due to an excess of solvent remaining in it. Over-baking the sample, instead, will increase the sensitivity to UV light and, in severe cases, may destroy the photo active component and reduce the solubility of the PR in the developer. for s-1813 soft-baking is carried out at 110°C.

One of the most important steps in the photolithography process is mask alignment. A mask or "photomask" is a square glass plate with a patterned emulsion of metal film on one side. The mask is aligned with the substrate, so that the pattern can be transferred onto its surface. The next step is exposing the sample to UV light, using a mask to create both exposed and unexposed portions of PR. The areas that are exposed to the UV light will undergo the chemical reaction which allows the photoresist to be soluble in the developer. This process is of paramount importance in photolithography in order to let it be an efficient process. In this respect, it is important to expose the PR correctly in terms of the right amount of time. If PR is exposed for a short time, then it will not react enough with light and there will be some areas of resist not removed after the development procedure (Figure 3.2 a). On the other hand, long exposure could make the protected areas exposed due to diffraction and focus resolution (Figure 3.2 b).



Figure 3.2: Drawbacks caused by under exposure (a) and long lasting exposure (b) to UV radiation.

The development allows obtaining the removal of unexposed PR. Again, the choice of the right development-time is important in order to overcome some limitations. In fact over-development causes the removal of less acidic parts too, even if they are removed slower. This causes the effect depicted in Figure 3.3.



Figure 3.3: drawbacks caused by incorrect development-time.

Developers originally often contained sodium hydroxide (NaOH), but Metal-ion-free developers such as tetramethylammonium hydroxide (TMAH) are now used. For S-1813, the developer MF321 is used.

Hard-baking is the final step in the photolithographic process. This step is necessary in order to harden the photoresist and improve adhesion of the photoresist to the wafer surface.

### 3.4 Plasma Etching: surface cleaning procedure.

Plasma cleaning involves the removal of impurities and contaminants from surfaces through the use of an energetic plasma created from gaseous species. Gases such as argon and oxygen, as well as mixtures such as air and hydrogen/nitrogen are used. The plasma is created by using high frequency voltages (typically kHz to >MHz) to ionize the low pressure gas (typically around 1/1000 atmospheric pressure), although atmospheric pressure plasmas are now also common [7].

In a plasma, gas atoms are excited to higher energy states and also ionized. As the atoms and molecules 'relax' to their normal, lower energy states they release a photon of light, this results in the characteristic "glow" or light associated with plasma.

Different gases give different colors. For example, oxygen plasma emits a light blue color.

A plasma's activated species include atoms, molecules, ions, electrons, free radicals, metastables, and photons in the short wave ultraviolet (vacuum UV, or VUV for short) range. This 'soup', which incidentally is around room temperature, then interacts with any surface placed in the plasma.

If the gas used is oxygen, the plasma is an effective, economical, environmentally safe method for critical cleaning. The VUV energy is very effective in the breaking of most organic bonds (i.e., C–H, C–C, C=C, C–O, and C–N) of surface contaminants. This helps to break apart high molecular weight contaminants. A second cleaning action is carried out by the oxygen species created in the plasma ( $O_2^+$ ,  $O_2^-$ ,  $O_3$ , O, O<sup>+</sup>, O<sup>-</sup>, ionized ozone, metastable excited oxygen, and free electrons). These species react with organic contaminants to form H<sub>2</sub>O, CO, CO<sub>2</sub>, and lower molecular weight hydrocarbons. These compounds have relatively high vapor pressures and are evacuated from the chamber during processing [6]. The resulting surface is ultraclean.

If the part to be treated consists of easily oxidized materials such as silver or copper, inert gases such as argon or helium are used instead. The plasma activated atoms and ions behave like a molecular sandblast and can break down organic contaminants. These contaminants are again vaporized and evacuated from the chamber during processing.

#### **3.5** Electrical characterization: I-V and C-V measurements.

The current-voltage characterization was performed to test the rectification properties of the heterojunctions and the efficiency of the cells. The measurements were carried out by a Keithley 2635 Source Measure Unit which allows to generate current in the  $10^{-13}$ - $10^{0}$  A range and to measure the voltage drop at the ends of the device. The

automatic acquisition of the IV data is driven by a home-made software. The IV characteristics are obtained by increasing the current step by step and by measuring the corresponding voltage values. The program allows the operator to determine, through the fitting of the IV characteristic, the saturation current and the ideality factor. Moreover by the analysis of the slope of the forward characteristic it is possible to have information about the main transport mechanisms through the junctions.

The measurements were performed both in the dark and under illumination using a Abet sun 2000 solar simulator (1.5 AM 25°C). From the IV characteristic under illumination we determined the open circuit voltage, the short circuit current, the fill factor and the efficiency of the cell.

Capacitance versus voltage measurements were carried out to obtain information about the free carrier concentration profiles in the CIGS active layer, that is in the less doped region of the n+ZnO/CdS/p-CIGS heterojunction.

It is well known that for a n+/p heterojunction, the free carrier acceptors profile p(x) is given by:

$$p(x)=2e/q [d(1/C^2)/dV]^{-1}$$
 (3.5)

where C is the capacitance of the junction, e the dielectric constant of CIGS and x [x=W(V), W=depletion layer width] the distance from the junction interface.

However, C depends not only on the free carrier density, but also on the deep levels present in the space charge region of the junction. Indeed, when the deep levels are able to respond to the sinusoidal test signal, the measured capacitance C increases owing to the induced charge variation at the crossing point between the deep level and the Fermi level. The increase of capacitance is proportional to the deep level concentration and depends on the energy level position into the gap. In these conditions the p(x) profiles, determined on the basis of the previous formula, are no more correct and reliable p(x) profiles can be determined only provided that measurements are performed by using a test frequency  $2\pi\omega$  much higher than the carrier emission rate of the deep levels. Taking into account that the emission rate increases exponentially with increasing temperature, the above conditions can be obtained by decreasing the cell temperature and/or by increasing the test signal frequency.

In order to check the presence of deep levels in the depletion region of the junction and to fix the test frequency, preliminary capacitance versus frequency measurements (500 Hz-5 Mhz) at different temperatures were carried out. When no deep level or deep levels in very low concentration are present, the capacitance vs frequency remains constant and the capacitance (and as a consequence the p(x)) can be correctly measured at any frequency. In case of strong variations of C vs f, as it is commonly observed in CIGS –based solar cells, it is necessary to perform the measurements at low temperature and high test frequency, in a range of frequency where the capacitance remain constant and the time response of the deep levels is much longer than the period of the sinusoidal signal.

# **3.6 Transfer Length Method for contact resistance analysis.**

Contact resistance R*c* is considered an important figure of merit to evaluate the quality of an ohmic contact. If the specific contact resistance is not negligible and the current density through the area of the contact is not uniform due to the current crowding mechanism, the current tends to flow in the region with lower resistance. So an accurate measurement of the contact resistivity  $\rho_c$  is required.

This measurement can be performed by using the so called Transfer Length Method (TLM) [8]. To this aim a set of parallel contacts are prepared on the CIGS film and the resistance is measured between adjacent contacts. According to this method, the measured resistance R is given by:

$$R=2R_{C}+\rho_{s}L/W \qquad (3.6)$$

where  $R_C$  is the contact resistance,  $\rho_s$  is the sheet resistivity of the CIGS film, L is the distance between two contacts and W is the contact width.

R is then a linear function of L, so Rc can be obtained from equation (3.6) by extrapolating the R vs L straight line to L=0. Similarly, from the slope dR/dL it is possible to estimate  $\rho_s$  while for R=0 one obtains (Figure 3.4):

$$L=-2RcW/\rho_{s}=-2\sqrt{\rho_{c}}\rho_{s}/\rho_{s}=-2\lambda \qquad (3.7)$$

where  $\rho_c$  is the contact resistivity and  $\lambda = \sqrt{(\rho_c/\sqrt{\rho_s})}$ .



Fig 3.4: resistance values extrapolated using Ohm's law from recorded I-V curves vs. contact spacing [9].

# 3.7 Thermography.

Thermography is a technique suitable to be employed with the aim of analyzing shunts in solar cells [10]. Shunts in solar cells are a detrimental factor, dramatically reducing the device efficiency, consisting in structural defects where a strong power dissipation (and a consequent temperature increase) occurs due to a local increased current flow. The origin and the nature of shunts will be treated in detail in section 7.

The principle on which thermography operates is based on the fact that the matter emits radiation when its temperature is higher than 0 K [10].

The amount of emitted power depends on the temperature of the object, according to Stefan-Boltzmann equation:

$$W = \varepsilon \sigma T 4 (3.8)$$

where W is the emitted power,  $\varepsilon$  is the emission coefficient of the object,  $\sigma$  the Stefan-Boltzmann constant and T the temperature of the object expressed in Kelvin. It is clear that the higher is the object temperature, the more thermal energy is emitted. So, by collecting infrared images, it is possible to build a temperature map of a sample, showing the local distribution of temperature over the sample surface.

Even if infrared radiation is invisible to the human eye, due to its long wavelength, infrared images can be produced by using an infrared camera detecting the radiation and converting, then, it into an electric signal. The signal is then processed to produce an image where different colors correspond to different temperatures.

It is clear that infrared radiation can be collected by the camera from the ambient, so that some radiation can be reflected from the sample surface. For an opaque material, the emission coefficient  $\varepsilon$  and the reflectance  $\rho$  are linked by the formula:

#### $\epsilon + \rho = 1$ (3.9),

so a higher emission coefficient results in a better infrared image, being the reflectance reduced for high emission coefficients[8]. Moreover, for a better imaging it is required that the emission coefficient is uniform over the whole surface too.

### **3.8** Thickness measurements: profilometry.

The thin film thickness and the surface roughness were measured using a contact mechanical profilometer.

Contact profilometers are generally made of a diamond stylus that is first positioned in contact with the sample surface and then laterally moved while measuring the vertical stylus displacement as a function of position, which allows the surface roughness to be determined. A typical profilometer can measure vertical features with a resolution that can exceed 1 nm. The lateral resolution is controlled by the scan speed and is limited by the diamond stylus radius that in different systems ranges from 20 nm to 50  $\mu$ m, The stylus tracking force can range from less than 1 to 50 mg. This technique is direct and it does not require any modelization for data analysis, Film thickness can be determined by measuring the height of the step obtained by locally removing the film to be measured.

### References

[1] K. Wasa et al, Thin Film Materials Technology: Sputtering of Compound Materials, William Andrew, Norwich, 2004.

[2] H. Singh N. et al. Handbook of Thin Films, vol 5, 2001.

[3] www.tcbonding.com

[4] Handbook of Thin Film Deposition Processes and Techniques, 2001, chapter 8, 2001 William Andrew Inc.

[5] Jaeger, Richard C. (2002). "Lithography". Introduction to Microelectronic Fabrication (2nd ed.). Upper Saddle River: Prentice Hall.

[6] D. Mitzi, Solution Processing of Inorganic Materials, 2009, Wiley.

[7] M. Sugawara et al, Plasma Etching: Fundamentals and Applications 2002, Oxford University Press.

[8] A.Scorzoni et al., Metal /semiconductor contact resistivity and its determination from contact resistance measurements 1988.

[9] A.Diligenti, F. Pieri Appunti di Strumentazione e Misure per la Microelettronica UNIPI

[10] G.Guassorgues, Infrared thermography 1994, Chapman & Hall, London

# 4.Back contact molybdenum on SLG substrate

### 4.1 Molybdenum back contact

 $Cu(In_XGa_{1-X})Se_2$  (CIGS) thin film solar cells usually use molybdenum as the back contact electrodes in solar cell devices. The properties of thin film Mo is crucial for the performance of the solar cells based on CIGS[1].

The Mo is a transition element (group 6) with atomic number 42. In pure form Mo is a silver grey metal with Mohs hardness of 5.5. It has a melting point of 2623 °C, and it has one of the lowest coefficients of thermal expansion( $5x10^{-6}$  K<sup>-1</sup>) among commercially used metals [2].



Figure 4.1: Molybdenum crystal structure body centered cubic [3].

A variety of metal/CIGS contact have been investigated, considering Mo [4-8], Au[4-6-8,9], Pt[ 4-5,8], Al [6,10-11], Ni [6,7,9], Ag [6] and Cu [6]. Mo, Pt, Au and Ni back contacts show fairly reproducible low contact resistance to CIGS. However Au and Pt show a significant diffusion into CIGS film at 600°C, while the Mo at the same annealing treatments temperature has a much lower diffusion through CIGS absorber layer. Mo is preferable compared to Ni, Al, Pt because it is resistant to corrosion due to Se an S. The resistivity of Mo layer is one order of magnitude higher than bulk (5.5 x  $10^{-6} \Omega$ -cm).

Generally Mo back contact form a Schottky barrier to the CIGS absorber, but [12] it was shown that during CIGS deposition the Mo/CIGS contact becomes ohmic

because of a reaction between Mo and Se which leads to the formation of a MoSe<sub>2</sub> layer.

It was reported that properties of Mo films deposited by dc-magnetron sputtering depend on the sputtering parameters used such as Ar pressure and sputtering current [13,14,15]. In particular Mo films sputtered with high argon pressure are dense and under tensile stress, they adhere well to the glass but they have high resistivity, while those sputtered at low argon pressure are under compressive stress, they show porous microstructures, they have low resistivity but they adhere poorly to the SLG substrate. Thus single Mo layers don't show at the same time good adhesion and low resistivity. Scofield [13] proposed a procedure to realize two-layers Mo films changing Ar pressure during sputtering deposition. The first layer was deposited at high Ar pressure (10 mTorr) to obtain a good adhesion onto SLG substrate, while the second layer was deposited at low pressure (1 mTorr) to have a film with low resistivity. These bilayer films passed the tape-test for adhesion and have low resistivities (12- 15  $\mu\Omega$  cm).

Mo thin films were deposited also using sputtering RF by Jubault et al [16] who confirmed the importance of a high pressure deposited adhesive layer in DC mode, while RF sputtering permits to overcome elimination problem for a wide range of pressure. Furthermore, the influence of the pressure over the physical properties of the molybdenum was stronger in DC sputtering, while in RF sputtering, electrical and optical properties of the films are less influenced by the process parameters.

Mo films obtained by e-beam evaporation [17-18] show a dense, tightly packed, small-grain microstructure which results in lower CIGS solar cell efficiencies compared to sputtered Mo due to the reduced Na diffusion from the SLG to the CIGS absorber.

### **4.2 Experimental details**

Mo thin layers were prepared onto 2.5 cm x 2.5 cm x 1 mm soda lime glass (SLG) substrate using an Edwards Auto 306 DC sputtering system at different working Ar pressures, currents and powers. Before metallization SLG substrates were cleaned by sonicating in soap and deionized (DI) water, rinsing in hot acetone and ethanol and drying in nitrogen flux. Finally the SLG surface was treated with  $H_2$  plasma at 60 mTorr for 10 minutes.

The distance between the Mo target (99.95 % Testbourne Ltd, 3- inch diameter, 12.7 mm thick) and the SLG substrate was 15 cm. The following process was used for deposition of all Mo thin layers. The sputtering chamber is evacuated by rotative + diffusive pumps system to  $6 \times 10^{-6}$  mbar. The Ar was then introduced into chamber using a needle valve that allowed the pressure to be maintained at the desired value during the deposition process. We have deposited several Mo layer varying working Ar pressure from 4.4 x 10<sup>-3</sup> mbar to 2.1 x  $10^{-2}$  mbar, and varying current sputtering from 0.4 A to 0.95 A. Sample thickness was not measured directly, but based on calibration run was deposited a nominal thickness of 171 nm for Mo thin film monolayer and 360 nm for Mo thin film bilayers.

### 4.2.1 Mo film thickness measurement

Mo thickness layer was carried out using wet chemical etching, using photolitography pattern test. The films deposited was measurement using Alpha step profiler. On a 25 x 25 mm SLG substrate , by photolitography, a pattern has been realized; it will be after removed by chemical etching.

So we removed a part of Mo film and it was possible to measure the thickness between the Mo film and the glass. The necessary steps to realize test films are shown in fig. 4.2.



Figure 4.2: Steps measurement Mo film thickness

We made chemical attack proofs on a Mo film using different solutions to define the best attack resolution for a complete Mo removing.

- 1) HCl 37% + H<sub>2</sub>O solution ratio 1:1
- 2) HNO<sub>3</sub> 65% + HCl 37% solution ratio 1:1
- 3) Br<sub>2</sub> 0.2 M + KBr 0.1 M solution ratio 1:1

Solutions 1 and 2 weren't adequate because the first didn't shown a significant chemical attack, the second one shown an etching rate higher than 3,but at same time it has provoked a photoresist deterioration causing the complete Mo film removal on the total surface. Number 3 revealed to be the best. Etching rate  $\sim 1$  nm/sec allows to remove Mo from the area which is exposed at photolithographic processes.



Figure 4.3: Etching time Vs thickness Mo film

Ar pressure → Current	$4.4 \times 10^{-3}$ mbar	$1.3 \times 10^{-2}$ mbar	$2.1 \times 10^{-2}$ mbar
0.4 A		390 nm 0.1 nm/s	
0.8 A	200 nm 0.4 nm/s	385 nm 0.3 nm/s	660 nm 0.2 nm/s
0.95 A	215 nm 0.5 nm/s	400 nm 0.35 nm/s	

Table 4.1: Deposition rate measured during the metallization and thickness of the Mo film determined by profilometry. For all the samples a nominal Mo thickness of 170nm was deposited.

At a given  $I_{DCS}$  (e.g. 0.8 A), increased Ar P [13].increasing P the thickness increases in consequence of the film porosity increasing At a given pressure (e.g.  $1.3 \times 10^{-2}$  mbar) the deposition rate increases with  $I_{DCS}$ .

The morphological and structural characterization of Mo layers deposited with different Ar pressures and different currents was carried out using atomic force microscopy and Philips PW 1850 a diffractometer (XRD) with Goebel monochromator with resolution 0.001°.

The layer sheet resistance was measured using four probe measurement system in the van der Pauw configuration [19].

The Mo thickness layer was carried out using an alpha-step profilometer. The adhesion of Mo layer to SLG substrate assessed using tape test.

### 4.3 Results and discussion

#### **4.3.1 Structural and morphology Mo thin layer**

The first Mo thin film monolayer sample was deposited at high Ar pressure  $(1.3 \times 10^{-2} \text{ mbar})$  at 0.95 A DC sputtering current (I<sub>DCS</sub>), without heating, to have a good adhesion onto SLG substrate. The Mo thickness film is 400 nm. Preliminary Bragg-Brentano measurements were carried out and the intensity of the Mo main peak was determined.



Figure 4.4: XRD spectra Mo thin film prepared at  $1.3 \times 10^{-2}$  mbar with sputtering current of 0.95 A.

Figure 4.4 shows the XRD of a Mo thin film with (110) preferred orientation typical of cubic system [13]. Also other orientations in particular (221) and (220) are present and confirm that film obtained are Mo. The secondary phases are not present and in particular we do not observe  $MoO_3$  which would make insulating film [20].



Figure 4.5: Cross-section HAADF STEM images of CIGS solar cell made IMEM (a) and (b) Mo film bilayers.

The microstructure and morphology of Mo film bilayers deposited was examined by high-angle-annular-dark-field scanning transmission electron microscopy (HAADF STEM).

In fig. 4.5 is shown a section of CIGS/Mo/SLG structure. It was deposited a bilayer film Mo back contact. The first layer was deposited at 1.3  $\times 10^{-2}$  mbar Ar pressure with a normal thickness of 50 nm. The second layer was deposited varying the Ar pressure during the deposition up to a value of 4.4  $\times 10^{-3}$  mbar up to a thickness of 350 nm.

TEM cross-section images reveal:

- good adhesion of first Mo layer on SLG substrate.
- CIGS/Mo interface with no defects
- Good columnar structure of Mo films

Mo films grown at different Ar P show a different structure and morphology due to differences in film porosity during deposition.

Real thicknesses are 118 nm (1 layer) and 440 nm (second layer) according with thickness measures obtained at the profilometer. Dimensions of grains are from 20 up to 45 nm.

# 4.3.2 SLG substrate cleaning

Although bilayer Mo films are used as the first layer deposited at high Ar pressure favours Mo adhesion, back contacts were not found to systematically adhere to the SLG substrate. To achieve a reproducible and reliable Mo adhesion we considered different substrate preparation methods.

Two different cleaning procedures were used (table 4.2):

**Treatment 1**: substrates were rinsed in hot polar aprotic acetone and polar protic ethanol, sonicated in water soap solution, washed in deionized water and finally dried in blowing nitrogen. This procedure is expected to eliminate the possible presence of organic traces on glass surface by the use of organic solvents (polar aprotic acetone and polar protic ethanol).

**Treatment 2**: substrates were, sonicated in water soap solution, washed in deionized water, rinsed in hot polar aprotic acetone and polar protic ethanol and finally dried in blowing nitrogen. This process is characterized by the initial use of water with soap in an ultrasonic bath, followed by rinsing in hot organic solvents, contributes to eliminate organic residues on the surface, taking advantage of the high ethanol volatility during drying.

Treatment A	Treatment B	
rinsing in hot Acetone	sonicating in soap solution	
rinsing in hot ethanol	sonicating in deionized	
sonicating in soap solution	water	
sonicating in deionized	rinsing in hot Acetone	
water	rinsing in hot ethanol	
drying in N <sub>2</sub>	drying in N <sub>2</sub>	

Table 4.2: Treatments used to prepare the SLG substrates

Samples were then metallized in an Ar pressure of  $1.3 \times 10^{-2}$  mbar using I<sub>DCS</sub>=0.8 A. A non-treated sample previously metallized was considered for reference.

Sample Name	(A)	<b>(B)</b>	(C)
Treatments	None	Treatment 1	Treatment 2
I <sub>DCS</sub> (A)	0.5	0.95	0.95
Tape test		Fail	Pass

Table 4.3: Summary of treatments on SLG Vs Mo film adhesion

The Mo film does not adhere at all on the untreated sample (Figure 4.6 A), a major problem that prevents adequate adhesion being the presence of organic contamination on the surface. For sample B the adhesion is not sufficient to pass the tape test (Figure 4.6 B), while in sample C, adhesion was very good, even if it was found that results were not fully reproducible and metallization must be performed not later than few days after sample cleaning.



Figure 4.6: Mo film adhesion onto samples A, B and C.

Aiming at overcoming this problem, the aging effect was studied considering samples treated following different procedures where, after the same preliminary cleaning (sonication in soap solution followed by sonication in deionized water), sample were treated according to processes reported in Table (4.2). After fixed time intervals substrates were then Mo metallized by a bilayer film ( $I_{DCS}$ =0.95A), where the first layer was deposited in 1.3x 10<sup>-2</sup> mbar and the second in 4.4 x 10<sup>-3</sup> mbar Ar pressure. Adhesion was assessed by tape test soon after metallization. Figure 4.7 shows that up to 3 days after treatment good adhesion is obtained for all the samples. When time between treatment and metallization increases tape test on samples C ad D fails, while after 60 days adhesion is still very good only for the hydrogen treated sample. This suggests that usual and cheap solvent cleaning is effective in giving good Mo adhesion if substrates are metallized soon after cleaning, while hydrogen plasma treatments is the best suited for stable SLG substrates that can be successfully metallized even two months after treatment.

Sample	Treatment
С	rinsing in hot acetone for 30 s rinsing in hot ISOH for 30 s
	drying in blowing nitrogen
D	rinsing in hot ISOH for 30 s drying in blowing nitrogen
Е	Drying in blowing nitrogen H <sub>2</sub> plasma (600s, 100mTorr, 100W)
F	Drying in blowing nitrogen O <sub>2</sub> plasma (600s, 100mTorr, 100W)

Table 4.4: Processes used after preliminary cleaning



Figure 4.7: success or failure of tape test for adhesion on samples treated as described in text. Intermediate results between "pass" and "fail" represent partial removal of the Mo film.
## 4.3.3 Influence of the working Ar pressure

The influence of the Ar pressure on Mo film morphology has been discussed above, pointing out that a low Ar pressure gives a compact layer, while high Ar pressure results in a porous film. We studied by AFM the surface morphology of Mo films deposited at different Ar pressure. Figure 4.8 shows the AFM images of three Mo films grown at different work pressures (see Table 4.5), at constant current (0.8 A). It is noticeable that surface roughness increases with Ar pressure (Figure 4.9), while grain size decreases.

Sample	(A)	(B)	(C)
Working pressure (mTorr)	3.3	9.8	15.7
dare la P <sub>Ar</sub> in mbar			
Surface roughness (nm)	1.09	2.20	12.58

Table 4.5: Variation of the surface roughness as a function of the working Ar pressure.



Figure 4.8: AFM images of Mo single layers obtained at different working Ar pressure: (A) 3.3 mTorr, (B) 9.8 mTorr, (C) 15.7 mTorr.  $I_{DCS}$ =0.95A, nominal thikness=170 nm

This leads to increasing porosity with the consequent increase of the film thickness.



Figure 4.9: Roughness profile of Mo single layers obtained at different working Ar pressure: (A) 3.3 mTorr, (B) 9.8 mTorr, (C) 15.7 mTorr. I<sub>DCS</sub>=0.95A

As consequence of the influence of the Ar pressure on Mo morphology, Ar pressure is expected to affect also the Mo resistivity, which contributes to the cell series resistance. The attractive force (e.i. tensile forces between these grains) is inversely proportional to the intragranular space. At pressure decreasing we have a lower scattering of atomic species and so a film with a lower porosity because the area among Mo grains is smaller. When we have high pressure, the Mo film porosity increases and with it the thickness of obtained film too (about 600 nm)at the same current deposition conditions and times. The porosity increase can cause impurities incorporation of O2 and H2 and water vapour that can cause a structural morphological film modifications.



Figure 4.10 Mo film resistivity as a function of sputtering Ar pressure for two different  $I_{DCS}$ . Literature data are reported for comparison.

As expected Mo resistivity decreases when sputtering Ar pressure decreases, in agreement with the literature and with the fact that lowering Ar pressure leads to increasingly compact Mo layers. Scofield [13] shows resistivity data which are lower (about 10  $\mu\Omega$ / cm) because his system allows to reach Ar pressure of about 3.3 mTorr. After we deposited another Mo films series increasing sputtering current value up to 0.95 A, we can notice another resistivity decreasing up to 18  $\mu\Omega$ / cm for a pressure valor of 3.3 mTorr.

A resistivity increasing when Ar pressure increasing can be explained by average kinetic energy of the Mo atoms picked from the target decreasing (so their mobility decreases). Because of this, films show higher porosity and thickness. Confirmed by AFM images that shows a superficial roughness increasing when Ar pressure increases.

# 4.3.4 Influence of the sputtering current DC

Mo films deposited at an Ar pressure of 9.8 mTorr were after analyzed, varying sputtering current (table 4.rr) with value of 0.4 A (8), 0.8 A (b) e 0.95 A (c).

Working current DC (A)	0.40	0.80	0.95
Surface roughness (nm)	4.50	2.20	8.11

Table 4.6: Variation of the surface roughness in function of working DC current sputtering.

AFM images show an initial decrease of medium roughness when current increases. At current value of 0.95 A we can observe a roughness increasing up to 8.11 nm and an increasing of grains dimension too (still due to kinetic energy of Mo atoms. At low current value the medium rate (0.1 nm) is low and so we obtain films with an higher porosity and thickness.



Figure 4.11:The AFM images of Mo thin layer obtained at different working DC current sputtering: (a) 0.4 A, (b) 0.8 A, (c) 0.95 A.

In fig. 4.12 we compare medium roughness trends of films grown at different Ar pressure on a  $1\mu m \times 1\mu m$  area.



Figure 4.12: Roughness profile of Mo single layers of Mo thin layer obtained at different working DC current sputtering: (a) 0.4 A, (b) 0.8 A, (c) 0.95 A.

Medium roughness at high current value is higher because it increases depositing rate (0.35 nm) and so we obtain a grains density increasing. Low currents make Mo films with lower medium roughness. We can note that we obtain films with medium roughness lower than 2.20 nm when current value is 0.8 A. In figure 4.13 is shown resistivity trend in function of sputtering current.



Figure 4.13: Mo film resistivity as a function of current DC sputtering at 9.8 mTorr Ar pressure Literature data are reported for comparison.

As is reported from [21-22] we can note that at a current increase corresponds a lower resistivity. Experimental data in this thesis work show how , for an operative limit of sputtering typology of 1 A, resistivity decreases when current increases according with literature data. According with AFM data, when current increases, film porosity decreases and so we observe a resistivity decreases. Depositing a film with double thickness (720 nm) we obtain a resistivity decreasing up to about 100  $\mu\Omega$ / cm.

### 4.3.5 Bilayers Mo film deposition

Analyzing monolayer Mo films utilizing just one Ar pressure, we observe how they cannot have low resistivity and good adhesion at SLG substrate at the same time. Operating at Ar low pressure value resistivity decreases but the film shows a compressive stress that causes poor adhesion. Operating at high pressure value, having an high porosity, the film shows at the same time a tensile stress that allows a good adhesion on the substrate, but at the same time it shows an high resistivity unfitting to have high performances solar cells.

Because of this Scofield [13] proposes the realization of a multilayer Mo film operating at different pressures during depositing. Varying pressure value while depositing it's possible to obtain a film with a good adhesion on the substrate (high pressure) and a low resistivity (low pressure) at the same time. In figure 4.14 is shown how in Scofield [13] work bilayer film with double thickness of 1  $\mu$ m shows a resistivity comparable with monolayer films deposited at low pressure (about 500 nm).



Figure 4.14: Mo film resistivity as a function of sputtering Ar pressure. Comparison one layer and bilayer Mo film deposited in Scofield work [13].

In this thesis work bilayer Mo films were realized to optimize the back contact realization process for CIGS solar cells for having at the same time a good adhesion Mo onto SLG substrate and low resistivity.



Figure 4.15: Mo film resistivity as a function of sputtering Ar pressure. Comparison one layer and bilayer Mo film deposited. Literature data are reported for comparison.

Starting with the morphological and electrical analysis of Mo monolayer films, we chooses the best deposition conditions of bilayer films with a normal thickness of 350 nm. Before we deposited a film with a pressure of  $1.3 \ 10^{-2}$  mbar of nominal 50 ones to promote substrate adhesion. Pressure value has been varied during deposition and keep constant up to  $4.4 \ 10^{-3}$  mbar to deposit the second layer at low resistivity. The sputtering current has been maintained constant at value of 0.95 A during the entire deposition.

In (Figure 4.15) the resistivity trend of a bilayer film is shown in comparison with Scofield data. We can note that the trend is comparable and a film with a resistivity of about 30  $\mu\Omega$ /cm is obtained. The tape test confirms the adhesion of the Mo film on the SLG substrate.

Mo bilayers were realized varying the first contact layer deposited at 15.7 mTorr and 0.95 A.



Figure 4.16: Mo bilayers film resistivity as a function of first layer thickness.

Decreasing the thinckness of first layer, we can observe how total film resistivity decreases even if adhesion at SLG remains the same up to a thickness of 10 nm.



Figure 4.17: The AFM images of Mo thin bilayer obtained at different first layer thickness.

AFM images show how film roughness decreases with first Mo layer decreasing and with the increasing of the second layer grown at low Ar P (so less porous).

## 4.4 Conclusions

In this chapter we underline the optimization steps for Mo back contacts in CIGS solar cells. We studied morphological and electrical properties of Mo film grown by sputtering on SLG substrates.

A method for substrates cleaning was created which was revealed to be fundamental to have a good adhesion of Mo by using solvents and different processes. Treatments in  $H_2$  plasma were useful for SLG surface stabilization and we obtained good metallizations with and optimal adhesion even 2 months after treatment.

We analyzed the deposition influence of sputtering parameters on Mo films properties. Experimental data are according with literature data. Films grown at high Ar P have a good adhesion on substrate but high resistivity (80-100  $\mu\Omega$ /cm), and films grown at low Ar P have a poor substrate adhesion but a good resistivity decreasing (40-50  $\mu\Omega$ /cm). We realized double layers film varying Ar P during deposition so we can obtain films with both good adhesion and resistivity. The previous treatment of substrate clearing, allowed to decrease the Mo first layer obtaining ( with another resisivity decreasing up to 12-15  $\mu\Omega$ /cm bilayer films.

### References

- [1] J.R et al. J. Nano Electron. Phys 3 (2011) No 1, P. 766-775
- [2] J. Emsley, Nature's Building Blocks. Oxford University Press (2001). P.262–266. ISBN 0-19-850341-5.
- [3] www.periodni.com
- [4] F.A. Abou-Elfotouh et al.. J. Vac. Sci. Tech. A. 8(4) (1990) P. 3251-3254.
- [5] S. Ashou et al. Thin Solid Films, 226 (1993) P.129-134.
- [6] R.J. Matson et al. Solar cells, 11 (1984) P. 301-305.
- [7] D.W. Niles et al. Mat. Res. Soc. Symp Proc. 260 (1992) P. 299-304.
- [8] F.A. Abou-Elfotouh et al.. J. Vac. Sci. Tech. A. 7 (1989) P. 837-841.
- [9] E.Moons et al., J.Electron Mater., 22(3) (1993) 275-280.
- [10] C.L. Chan et al., j.Appl.Phys., 68(1) (1990) P.275-280.
- [11] D.K. rao et al., Phys.Status Solidi, 94 (1986) P.153-159.

[12] W.N. Shafarman et al., Proceeding of the 25<sup>th</sup> IEEE Photovoltaics Specialist Conference, Washington D.C., USA May 13-17, 1996, P.917.

- [13] J.Scofield et al., Thin Solid Film 260 (1995) 26-31
- [14] R. Noufi Conference Paper NREL/CP-520-39894 (2006)
- [15] L.Assmann et al., Applied Surface Science 246 (2005) 159-166
- [16] M. Jubault Solar Energy Material & Solar Cells 95 (2011) S26-s31.
- [17] Martinez Guillen Journal of Materials Processing Technology Vol.143-144 (2003)

[18] Fisher, D.C. et al. Photovoltaic Specialists Conference, 2005. Conference Record of the Thirty-first IEEE 3-7 Jan. 2005, 371 - 374

- [19] R. Chwang et al., Solid-State Electronics Volume 17, Issue 12, December 1974, 1217–1227.
- [20] C. V. Ramana et al., J. Vac. Sci. Technol. A 25, 1166 (2007).
- [21] A.Kadam et al., Jour. Vac.Sc.Tech 23 1197 (2005)
- [22] Jubault et al., Solar Energy Materials and Solar Cells 95 May (2011), S26–S31

# 5.Molybdenum back contact on alternative substrates

# 5.1 Building integration

The solar panels were obtrusive, did not fit in harmoniously with any home design and long discussions between spouses preceded any decision

Building integration of photovoltaic represents the road map towards the exploitation of renewable energy in the urban environmental. Today, the building integrated photovoltaic (BIPV) is an important segment of PV market, currently in very rapid expansion. Several installations have been carried out up to now, starting from that one realized in Aachen (Germany) in 1991 [1] obtained by integrating silicon photovoltaic panels into a wall facade. The first production line with a capacity of 5000 m<sup>2</sup> was realized in Germany by Pilkington in the end of 1993 [2], with an increase of capacity up to 50000 m<sup>2</sup>, reached in the 1999.

Today, only in China, the building energy consumption amounts to about 27.6% of total energy use. The BIPV is thought to play an important role in view of the increase of building energy consumption. BIPV can accomplish multiple tasks, as it can be used for thermal insulation tasks, as facade element and it can provide electricity.

The project PED4PV in collaboration with Marazzi S.p.a for ceramic substrate and CTG S.p.a, is devoted to the study and manufacturing of thin film solar cells based on CIGS. The use of nonconventional substrates (such as ceramics or cement) suitable to the building integration represent a central topic in the context of the project for cement substrate, as the substrates can act as finishing touches and covering materials in building while they are contemporary exposed to the solar radiation.

The main obstacle to be overcame in that kind of applications is the optimization of the pre-treatment processes of the building surfaces, both ceramic and cement, in order to make them appropriate to the photovoltaic fictionalization through direct deposition of thin films by chemical or physical methods. Beyond the problem of substrate surface porosity and roughness, the vacuum conditions and the temperatures achieved during the deposition and production steps, can activate diffusion and contamination processes of the functional layers deposited which need to be solved.

## 5.2 Ceramics alternative substrate

A ceramic is an inorganic, non-metallic, often crystalline oxide, nitride or carbide material. Ceramics are mechanically brittle, hard, strong in compression and weak in tension.

Ceramics stone tile are obtained by the action of heat and subsequent cooling on a mixture of clay and sand quartziferous materials baked in ovens at 1220°C for 30-60 minutes. After cooling, a hard material, insoluble in water and with peculiar chemical and mechanical properties, is obtained.

In general, ceramics do not show the required quality in terms of morphological features and processing conditions for thin film photovoltaics application. In particular, it is required on one hand that ceramics have to endure high vacuum conditions ( $10^{-5}$ - $10^{-6}$  mbar) and temperatures ranging between 250 and 400°C, while on the other hand they have to show compatibility with thin film technology in terms of their surface morphology.

## 5.2.1 Results and discussion

At first the roughness and surface morphology of traditional ceramic tiles were analyzed using both an alpha step profilometer and a SEM (scanning electron microscope) and compared with SLG substrate. Tiles showed a surface roughness of few nm (Figure 5.1), which is comparable with that of SLG (Figure 5.2). However, hollows as deep as several  $\mu$ m, (up to ~10 $\mu$ m) were observed all over the surface (Figure 5.1)



Figure 5.1: Roughness of traditional ceramic tile. Vertical scale (a)  $5\mu$ m/cm, (b)  $0.2 \mu$ m /cm. Horizontal scale 200  $\mu$ m/cm.



Figure 5.2: Roughness of glass. Vertical scale 0.5 µm/cm. Horizontal scale 200 µm/cm.

The roughness values obtained by scanning the tile surface show the following features:

- -Average roughness (excluding dips) of a few tens of nanometers;
- No extremely high peak values found;
- Average values of the dips is about 500 nm;
- Maximum value of the dips is 11.5 microns.
- Roughness unchanged after treatment under vacuum;

SEM analysis highlighted some areas with a low and uniform roughness together with deep pits, as detected by the profilometer. An average lateral size of about 5  $\mu$ m and a maximum of 10-20  $\mu$ m were estimated for the pits. From SEM images the pit density was also been estimated, providing a relatively high value of about 500/mm<sup>2</sup> (Figure 5.3)



Figure 5.3: SEM image of a traditional ceramic tile.



Figure 5.4: SEM image of a traditional ceramic tile.

A higher magnification of the electron microscope (4000X) clearly shows particularly marked lines on the surface likely related to the production process.

The surface quality of these tiles was not suitable for thin films cell fabrication, as it would be very difficult to produce continuous and homogeneous films on surfaces with such a morphology. As reported in the paper by [3], not perfectly smooth substrates are considered the main cause of the collapse of the performance of absorbing materials used in the field of photovoltaics for the following reasons:

- Cusps related to the roughness of the substrate act as nucleation centers for the materials during their growth and their presence causes the nucleation of many grains with a consequent excess of grain boundaries; these grain boundaries are equivalent to extended recombination centers whose effect is reflected in a low conversion efficiency for solar cells.

- High roughness of the substrate greatly increases the surface layer between absorber and the metal surface of the lower Mo contact, causing thus an higher probability of metal ions migration.

- The peaks of the substrate higher than 500 nm are dangerous because, once covered by the layer of Mo, they can penetrate inside the layer CIGS absorber forming a series of shunt resistors due to the absence of an electrical contact;

- Holes higher than 1  $\mu$ m cannot be covered by the deposition of thin films. In fact, it would take several  $\mu$ m of material to smooth out perfectly these imperfections, causing then a considerable increase in costs and production time.

Furthermore, in presence of so high roughness values, the control of the Mo layer uniformity turns out to be problematic as some cracks could be easily created on the film surface. As a result, uncovered areas of the substrate could favor the diffusion of a large number of contaminants, thus affecting the device performance. In order to eliminate the presence of deep cavities, scratches and grooves on the surface and obtain a smooth substrate, Marazzi's Group used the so called "third fire" decoration process. In this process, a second baking at 1060 °C (temperature lower than that required for ceramics preparation) was carried out after glazing, so that an over layer of glass was formed on the surface, so that irregularities due to the first baking were expected to be avoided.

In the first attempt, a process already consolidated, exploiting a particularly porous support for the substrate, was used. The reduction of pit number and depth indicated the beneficial effect of the "third fire" process, but surprisingly some pinnacles with base diameter of ~100 nm and height between ~100 nm and a few  $\mu$ m appeared (Fig.5.5), being these pinnacles rather numerous.



Figure 5.5: Roughness of ceramic stoneware tile with glassy coating Vertical scale  $1\mu$ m/cm

The roughness values obtained by scanning the sample surface show the following features:

- Average roughness of few hundred nm;

- Significant decrease of the pit concentration, with depth in the few hundred nm range.



Figure 5.6 Roughness profiles measure on gres porcellanato tiles (vertical scale= $5\mu$ m/cm, horizontal scale= $200\mu$ m/cm)

SEM investigation showed that pinnacles observed by profilometry were to be ascribed to particles spread over the tile surface and partially embedded into the glaze (Figure 5.7)



Figure 5.7: SEM images obtained on gres porcellanato tiles after a single third fire process

In order to enhance the surface quality a cycle of three baking steps in "third fire" decoration process was performed. The low average roughness was preserved by this treatment, but pinnacles were still present (Fig.5.8), with heights comparable to the singly baked sample (Fig.5.6), although their concentration was slightly reduced to about  $50/ \text{ cm}^2$ . It is worth noting that pinnacles were surrounded by dips.



Figure 5.8: Roughness profiles measure on gres porcellanato tiles (vertical scale= $2\mu$ m/cm, horizontal scale= $200\mu$ m/cm)

SEM investigation showed that the three backing steps was effective in decreasing the particulate size (Fig.5.9 a), and clearly pointed out that pinnacles originate from particles that progressively sink into the glaze (Fig.5.9 b). This observation allowed us to conclude that the poor surface morphology was related to dust present in the production line where tiles were treated.



Figure 5.9: SEM images obtained on gres porcellanato tiles after a single third fire process

In order to improve the environmental cleanliness during the third fire treatment a muffle furnace was then used. The roughness profiles of these samples show a general improvement in the average roughness (Figure 5.10 a and b), even if some few hundred nm high pinnacles are detected with surface density of  $\sim 10/\text{cm}^2$ ,



(Figs.5.10 c and d). Few large and rather shallow dips (surface density of 10-20/ cm<sup>2</sup>, few hundred nm deep and few hundred  $\mu$ m wide) were also found (Figure 5.10 d).

Figure 5.10: Roughness profile with glassy coating 1mm. Vertical scale is a)  $0.5 \mu$ m/cm, b)  $0.2 \mu$ m/cm, c)  $2 \mu$ m/cm, d)  $5 \mu$ m/cm. Horizontal scale= $200 \mu$ m/cm

SEM images show a rather smooth surface with some structures originating the holes and pinnacles observed in the roughness profiles. These defects are likely related to the particulate partially immersed in the glaze, which points out that using a muffle furnace guarantees improves the tile surface quality but process cleanliness must be further improved.



Figure 5.11 SEM images obtained on ceramic with glassy coating 1 mm

The last tile series was prepared by using a muffle furnace combined with a coating glaze characterized by a lower melting temperature which was expected to hinder the inclusion of particulates. The surface roughness of these samples was slightly worse than the previous series, but pinnacles and dips were no more observed, which makes these tiles suitable for thin film cell preparation.



Figure 5.12: Roughness profile gres porcellanato with coating glaze prepared in muffle furnace . Vertical scale is a)  $0.5 \mu$ m/cm, Horizontal scale=200 $\mu$ m/cm

SEM analysis confirmed the good quality of the surface in these last series, since particles shown in figure 5.13 are due to dust likely deposited during the courier transport.



Figure 5.13 SEM images gres porcellanato with coating glaze prepared in muffle furnace

Given the good surface quality of these samples, their compatibility with vacuum processes was tested and it was found that pressures lower that  $5 \times 10^{-6}$  mbar could be achieved.

The tiles were then prepared for the Mo deposition by the process described in Table 5.1 and Mo was deposited following the procedure discussed for glass substrates. The

Mo films showed a good adhesion, as observed by tape test. This indicates that these gres porcellanato slides could be used for GIGS solar cell fabrication.

Steps	Treatment
1	Sonication in soap water solution
2	Sonication in ethanol
3	Drying in blowing nitrogen
4	H2 plasma 60 mTorr 10 min

Table 5.1: Four steps procedure for surface treatment of ceramic samples before sputtering deposition of molybdenum back contac



Figure 5.14 SEM Ceramic sample with Mo film deposited by sputtering

# 5.3 Cement alternative substrate

In this thesis work made in collaboration with Italcementi in the context of project PED4PV, it was checked the feasibility of realizing cementitious substrates to be utilizez in building integration. Those cementitious substrates must act as substrates for CIGS thin film deposition in order to build up solar cells active layers. In particular, cement samples realized were fabricated by using different conditions (i.e. standard method, using polymeric coating and changing the composition of cement amalgam). The compatibility of the surface of the cement samples for Mo growth, acting as back contact of the solar cells, was checked by the morphological point of view and a surface treatment process was developed for the deposition of Mo thin films by sputtering.

It is worth to note that whitin PED4PV project the composition of cements used as substrates, and the subsequent realization by leakage, still stays hidden by production secret.

In the most general sense of the word, a cement is a binder, that is a substance that sets and hardens independently, binding other materials together. Cement used in buildings characterized as hydraulic or non-hydraulic. Hydraulic cements (e.g., Portland cement) harden because of hydration, chemical reactions that occur independently of the mixture's water content; such cements can harden even underwater or when constantly exposed to wet weather. The chemical reaction that results when the anhydrous cement powder is mixed with water produces not water-soluble hydrates. Non-hydraulic cements (e.g. gypsum plaster) must be kept dry in order to retain their strength.

The most important use of cement is the production of mortar and concrete—the bonding of natural or artificial aggregates to form a strong building material that is durable in the face of normal environmental effects. Concrete should not be confused with cement, because the term cement refers to the material used to bind the aggregate materials of concrete. Concrete is a combination of a cement, water and aggregates (gravel and sand). Cement is made by heating limestone (calcium carbonate) with small quantities of other materials (such as clay) at a temperature of 1450 °C in a kiln, giving rise to a process known as calcination, whereby a molecule of carbon dioxide is released from the calcium carbonate to form calcium oxide, or quicklime. Quicklime is then blended with the other materials one have to include in the mix in order to obtain the final product. The resulting hard substance, called 'clinker', is then ground with a small amount of gypsum into a powder to make 'Ordinary Portland Cement', the most commonly used type of cement (often referred to as OPC). Portland cement is a basic ingredient of concrete, mortar and most non-specialty grout. As pointed above, the most common use for Portland cement is in the production of concrete. As a construction material, concrete can be cast in almost any shape desired, and once hardened, can become a structural (load bearing) element. Portland cement may be grey or white.

Non-Portland hydraulic cements are introduced below:

- Pozzolan-lime cements. Mixtures of ground pozzolan and lime are the cements used by the Romans, and can be found in Roman structures still standing (e.g. the Pantheon in Rome). They develop strength slowly, but their ultimate strength can be very high. The hydration products that produce strength are essentially the same as those produced by Portland cement.
- Slag-lime cements. Ground granulated blast furnace slag is not hydraulic on its own, but is "activated" by addition of alkalis. They are similar to pozzolan lime cements in their properties. Only granulated slag (i.e. water-quenched, glassy slag) is effective as a cement component.

Supersulfated cements. These cements contain about 80% ground granulated • blast furnace slag, 15% gypsum or anhydrite and a little Portland clinker or lime as an activator. They produce strength by formation of ettringite, with a strength growth similar to a slow Portland cement. They exhibit good resistance to aggressive agents, including sulfate. Cement sets or cures when mixed with water which causes a series of hydration chemical reactions. The constituents slowly hydrate and crystallize; the interlocking of the crystals confers to the cement its strength. Maintaining a high moisture content in cement during curing increases both the speed of curing and the final strength. Gypsum is often added to Portland cement to prevent early hardening or "flash setting", allowing a longer working time. The curing time varies depending on the mixture and environmental conditions; initial hardening can occur in as little, that is about twenty minutes, while full cure can take over a month. Cement typically cures in a lapse such that it can be put into service in a range of time varying between 24 hours and one week

## 5.3.1 Results and discussion

As received samples were tested using a methodical procedure aimed to characterize the surface and define the cement substrate compatibility to thin films deposition and particular Mo back contact.

The analyzed samples are obtained by stripping the mixture in a rectangular shape molds with dimension of 76 mm x 26 mm.

The following tests have been carried out:

- a) Superficial roughness analysis of the sample with alpha-step profilometer;
- b) Vacuum treatment to check substrate compatibility with vacuum regimes used to deposit several layers constituting the photovoltaic cell;
- c) Samples pretreatment to deposit the Mo contact by sputtering.

Samples under analysis are made hydrating the cement mixed up with polymer fibers, aimed to increase the adhesive and mechanical properties of the cement mixture

Fiber-reinforced concrete (FRC) is a concrete containing fibrous material which increases its structural integrity. FRC contains short discrete fibers that are uniformly distributed and randomly oriented. Fibers include steel fibers, glass fibers, synthetic fibers and natural fibers – each of which lending peculiar properties to the concrete. In addition, the character of fiber-reinforced concrete changes upon concretes variation, fiber materials, geometries, distribution, orientation, and densities.

Fibers are usually used in concrete to control cracking due to plastic shrinkage and to drying shrinkage. They also reduce the permeability of concrete, reducing thus the bleeding of water. Some types of fibers produce greater impact–, abrasion–, and shatter–resistance in concrete. Generally fibers do not increase the flexural strength of concrete, and so they cannot replace moment–resisting or structural steel reinforcement. Indeed, some fibers actually reduce the strength of concrete.

Polymeric fibers can also improve mix cohesion, improving pumpability over long distances, improve freeze-thaw resistance, improve resistance to explosive spalling in case of a severe fire, improve impact resistance and increase resistance to plastic shrinkage during curing.

Analyzing a sample area of about  $0.12 \text{ cm}^2$  we can observe the presence of pits, whose depth can vary between 200 nm and 1  $\mu$ m (figure 5.15). The width of these pits ranges around 200-300 nm. This distribution is homogeneous on the whole sample surface, making the traditional composed cement hard to be used as substrate for thin film solar cells. In fact the presence of this pits can create shunts and short circuits in a p-n junction structure.



Figure 5.15: Roughness profiles on tradizional cement (vertical scale= $0.2\mu$ m/cm, horizontal scale= $200\mu$ m/cm).

Although cement samples made by traditional composition are not suitable by the morphological point of view as substrate for building integration, they have been used to create a technological process, to check the compatibility to vacuum regimes and surface cleaning treatments and, finally, to test the feasibility of a Mo thin film deposition.

Keeping in mind that cement under the chemical point of view is a mixture of silicates, calcium and calcium aluminates, the surface cleaning treatments based on acids or bases in solution cannot be carried out, as these solutions can provoke the dissolution of the amalgam with consequent samples usability.

For this reason, two cleaning procedures were made:

Treatment	Step	Surface sample	Initial	Final	Weight
			Weight	Weight	Change
			<b>(g</b> )	( <b>g</b> )	(%)
a	Ultasonic bath	Bad surface	17,59	18,17	3,30%
	Soap solution				
	DI Water 10 min				
	Nitrogen flux				
b	Ultrasonic bath	Good surface	18,00	18,67	3,70%
	Ethanol 10 min				
	Nitrogen flux				

Table 5.2: Steps procedure for cement surface treatment

The treatment labeled as (a) in Table 5.2 caused a partial surface deterioration, due to the treatment made with a soap solution, compromising the suitability for Mo thin film deposition. On the contrary, no substantial modification of sample surface roughness upon performing the treatment labeled as (b).

For those samples a weight gain after treatments has been observed, due to cement porosity which holds cleaning solvents with consequent problems of degassing in vacuum chamber.

The vacuum treatment, always aimed to check the substrate compatibility with deposition procedures, did not allow to reach the vacuum levels lower than  $10^{-5}$  mbar, whereas the Mo metallization requires at least a vacuum level of  $5 \times 10^{-6}$  mbar. Moreover, PED deposition requires even a lower background vacuum, of about  $10^{-7}$  mbar.

Despite the surface preparation procedures did not give good results, a Mo thin film deposition was carried out on two samples, one without the superficial treatment (Figure 5.16 a) and the other one after ethanol treatment (Figure 5.16 b). The degassing in vacuum chamber of residual solvent molecules hold by cement porosity,

makes the Mo deposition process really difficult because it does not allow a good control in growth parameters.



Figure 5.16: Adhesion Mo thin film on traditional cement: (a) without the superficial treatment, (b) after ethanol treatment.

The treatment in ethanol needs two fundamental aspects in order to favor a good substrate adhesion of a Mo film deposited by sputtering: a good superficial cleaning with resituates elimination and the preservation of the surface features upon cleaning, without any substantial modification found in samples treated for instance with soap water (causing a surface degradation). However the complete elimination of solvent after the cleaning is a fundamental aspect to avoid degassing problems in vacuum chamber; we consequently obtain harder vacuum regimes so that an optimal conditions for a good film deposition is guaranteed.

Three samples were treated in ethanol for 10 minutes and were then annealed to promote the complete solvent elimination. In table 5.3 the weight variations corresponding to a given treatment are shown. Besides a long lasting (3 hours) hot plate treatment at 35 °C, it has been considered the possibility of a shorter treatment (10 minutes) at higher temperatures (90°C). As it is evident in table 5.3, both treatments allowed to obtain the evaporation of the absorbed solvent, recovering the initial weight.

Samples	Initial Weight (g)	Weight after clearing surface (g)	Treatment	Final Weight (g)
1	17.11	17.55	90°C for 10 min	17.11
2	19:51	20.06	35°C for 3 hours	19.54
3	19.90	20.46	90°C for 10 min	19.90

Table 5.3: Annealing treatment on cement sample.

The samples were then submitted to a vacuum treatment to check the compatibility with the deposition processes. Now there is not an high degassing in growth chamber anymore. As a consequence, the expected vacuum value of about  $6.0 \times 10^{-5}$  mbar was reached.

Samples	Treatments	Tape test
1	Ethanol cleaning + stove annealing 90°C	fail
	10 min	
2	Ethanol cleaning + hot plate annealing 35°C 3 ore	fail
3	Ethanol cleaning + stove annealing 90°C 10 min	fail

Table 5.4: Different annealing treatments on cement substrate.

A Mo bilayer film was deposited by sputtering the first layer at a base Ar pressure of about  $1.3 \times 10^{-2}$  mbar, followed by a second layer deposited at an Ar pressure of 4.4 x  $10^{-3}$  mbar. The tape test evidenced that the Mo film adhesion on cement substrates treated on hot plate has not been fulfilled (Table 5.4), even if an enhancement of Mo

adhesion degree has been noticed compared to the adhesion on samples treated only with ethanol, without recurring to other thermal treatments.

The removal of just a little part of metallization has been observed when the tape test has been performed in a slow way, while a much more marked Mo film removal on large areas has been observed upon a "tear" like tape test (Figure 5.17a-b). Sample 1 (treated in stove at 90 °C) shows a better Mo adhesion compared to sample 2 ( treated on hot plate t 35°C). In order to investigate if the origin of such difference is due to the cement formula or to the treatment at 90°C the metallization of sample 3, which differing from the sample 2 only for the thermal treatment (90°C for 10 min) has been carried out. The results obtained on this last sample are comparable with the ones obtained on the homologous sample treated at 35°C, underling that the different Mo adhesion is probably due on sample nature itself, that is both the cement composition and surface morphology.



Figure 5.17: Adhesion Mo thin film on cement substrate after hot plate thermal treatment35°C.

The surfaces of conventional building materials (concrete, lime, gypsum, gypsum fibreboard, wood and other surfaces) need to be improved. Protective-decorative polymer coatings are most often applied for this purpose. The composition of the coating components depends on the operation conditions (air and water environment, aggressive air environment, low and high temperatures). According to the chemical nature of the basic film-forming component, the polymer coatings are classified as epoxy, acrylate, polyvinyl acetate, polyester, polyurethane, rubber, silicone, etc. The choice of the system to be applied is based on the net cost, ecological effects and durability of both the coating and the substrate. In the present case the latter aspects are affected by concretes composition. The durability, in particular, represents a complex of properties including adhesion, mechanical properties, porosity, water permeability, temperature resistance, and so on. Of course, adhesion is one of the most demanding, important properties because t represents the direct expression of the coating adherence to the substrate. In order to obtain a cement surface potentially useful for building integration, GTC provided samples with traditional composition but covered by a polymeric layer. This layer should enhance the surface morphology, reducing the presence of pinnacles.



Figure 5.15: Roughness profiles on cement with polymeric coating: (a) vertical scale= $0.25\mu$ m/cm, horizontal scale= $200\mu$ m/cm, (b) vertical scale= $0.25\mu$ m/cm, horizontal scale= $20\mu$ m/cm.

By scanning an area of  $0.10 \text{ cm}^2$  by means of the taly step, an average roughness lower than  $1\mu m$  has been observed, lower than that showed by samples made of

traditional cement. Extending the horizontal scale, it is evident that the roughness profile shows a "soft" trend, without the presence of many pits. For this reason, it can be argued that this area could fit as substrate for a Mo layer deposition.

The surface clearing treatments in ethanol for 10 minutes have underlined a weight gain of the sample and a macroscopic deterioration on the surface due to an attack of the polymeric mixture by ethanol. For this reason it has been chosen to carry out a surface treatment using only a nitrogen flow. The resulting vacuum regimes were suitable for Mo thin layer deposition, as they reached vacuum level was lower than 10<sup>-5</sup> mbar. This is due to the fact that the sample is now chemically untreated and so it is no more subjected to release impurities and resituated in deposition chamber. A Mo bilayer film deposition test shows a good adhesion on the polymeric surface too.

Sample	Treatment	Tape test
1	Nitrogen flux	pass
	-	

Figure 5.19: Mo film adhesion on the cement with polymeric coating substrate.

The use of a polymeric coating allowed to obtain a cement sample with a surface almost good for a Mo film deposition. However this deposition implies one more step under the technological point of view, with a consequent increase of costs for the realization of substrates fitting with building integration. This technological solution does not allow the use of the acquired methods (surface treatments before deposition of Mo thin film) even if a good adhesion has been observed.
The subsequent solution proposed by CTG consists in realizing samples made of the traditional cement with the addition of waterproofing agents in the percentage of 0.30 % for the sample (a) and of 0.15% for the sample (b).



Figure 5.20: Roughness profiles: (a) waterproofing agents in the percentage of 0.30 % vertical scale= $0.25\mu$ m/cm, horizontal scale= $200\mu$ m/cm, (b) waterproofing agents in the percentage of 0.15 % vertical scale= $0.25\mu$ m/cm, horizontal scale= $200\mu$ m/cm.

Further tests on surface morphology were performed on two samples by an alpha-step profilometer with an ocular area of about  $0.10 \text{ cm}^2$  (Figure 5.20 a-b). The samples showed an average roughness lower than 500 nm, evidencing the absence of pits and particularly deep holes. These substrates could then result suitable for thin film layers deposition.

The clearing treatment on samples surface are always made by an ethanol ultrasonic bath followed by a drying procedure in nitrogen flow. The samples were weighted before and after the treatment in order to check the extent of ethanol absorption and desorption occurring on long timescales.

Sample	ample Initial Weight		Weight	
	(g)	(g)	Change (%)	
(1)	23.83	24.11	+ 1.17	
(2)	18.99	19.37	+ 2.00	

 Table 5.5: Cleaning surface treatment and relative weight variation.

The gain in weight of the samples under analysis underlines that they absorb the solvent used in clearing processes even if this increase is lower than the one of samples made by both traditional cement and polymeric coating. Even in this case there are not macroscopic modifications after the treatment. A treatment in hot plate at 35°C for 3 hours has been carried out to obtain the complete evaporation of absorbed solvent, recovering in this way the initial weight.

Samples	Initial	Weight after	Treatment	Final Weight
	Weight	clearing		(g)
	(g)	surface (g)		
(1)	23.83	24.11	35°C for 3 hours	23.78
(2)	18.99	19.37	35°C for 3 hours	18.99

Table 5.6: Thermal treatments and and relative weight variation.





Figure 5.21: Tape test adhesion Mo thin film.

The Mo film adhesion underlines an enhancement with respect to that obtained in the cases previously described, even if adhesion of Mo films on samples is not adequate yet, as it has been shown by tape test (Figure 5.21 a). In particular the sample (b) showing the worst superficial morphology, did not show the detachment in large metallization areas, while in other sample the tape tests showed how Mo film has been removed on large areas.

## **5.4 Conclusions**

One of the most important and ambitious goals of PED4PV project was the possibility to deposit a thin film solar cell onto non conventional substrates like cements or ceramics. Beyond the problem of substrate surface porosity and roughness, the vacuum conditions and the temperatures achieved during the deposition and production steps, can activate diffusion and contamination processes of the functional layers deposited which need to be solved.

At first the roughness and surface morphology of traditional ceramic tiles were analyzed. The tiles showed a surface roughness of few nm but deep as several  $\mu$  (up to ~10 $\mu$ m) were observed. The surface quality of these tiles was not suitable for thin films cell fabrication, as it would be very difficult to produce continuous and homogeneous films on surfaces with such a morphology. In order to eliminate the presence of deep cavities, scratches and grooves on the surface and obtain a smooth

substrate, Marazzi's Group used the so called "third fire" decoration process using a second baking at 1060 °C so that an over layer of glass was formed on the tile surface. We were observed the reduction of pit number and depth indicated the beneficial effect of the "third fire" process, but surprisingly some pinnacles with base diameter of ~100 nm and height between ~100 nm and a few µm. subsequently in order to enhance the surface quality a cycle of three baking steps in "third fire" decoration process was performed. With this treatment the low average roughness was preserved, but pinnacles were still present. Further investigation showed that the three backing steps was effective in decreasing the particulate size and clearly pointed out that pinnacles originate from particles that progressively sink into the glaze. The last tile series was prepared by using a muffle furnace combined with a coating glaze characterized showed good quality of the surface and Mo thin film was deposited by sputtering. The Mo films showed a good adhesion, this indicates that these gres porcellanato slides could be used for GIGS solar cell fabrication.

In this thesis work the possibility of using a cement based substrate as a direct base for deposition of metallic layers, composing the CIGS solar cells for the building integration, has been evaluated. In collaboration with CTG some types of cement substrates have been tested in order to check their compatibility with thin film deposition processes, with a particular reference to Mo films acting as back contacts in solar cells. A method of investigation consisting in the analysis of the surface morphology aimed to understand its compatibility with conventional vacuum based deposition techniques has been adopted. After that, some surface cleaning treatments aimed to promote the adhesion of Mo film without recurring to aggressive plasma etching treatments, used generally for SLG, have been evaluated. Annealing aimed to remove residual solvents has been studied. Then test deposition of Mo bilayer have been carried out in order to check the samples compatibility with low vacuum regimes, lower than 10<sup>-5</sup> mbar, and the adhesion efficiency of Mo thin films with the substrates. Initially, samples made of traditional cement with a mixture of polymer fibers, promoting the stability of the samples presenting on their surface pinnacles and pits of some  $\mu$ m (unsuitable for the deposition of thin films), have been analyzed. The cleaning treatments have evidenced how ethanol is useful in order to avoid damages provoked by soap water solutions. The elimination of solvent by hot plate treatments at a low temperature (35 °C) has been enlighten to be good in order to favor Mo film deposition. Using cement substrate with polymeric coating should enhance the surface morphology, and we observed reducing the presence of pinnacles A Mo bilayer film deposition test shows a good adhesion.

## Reference

- [1](Benemann et al., Adv. Sol. Energy 13 (1999) 317).
- [2] Hestnes AG. Building integration of solar energy systems. Sol Energy 1999;67(4–6):181–7.
- [3] W.K. Batchelor, et al., Proceedings of the 29th IEEE Phot. Spec. Conf., New Orleans,

# 6. Technology for realization CIGS solar cells device

# 6.1 Copper mask for front contact evaporation

#### 6.1.1 Introduction.

The activity described in this thesis work has exploited a lot of technology for the production and related characterization of solar cell prototypes based on the glass/Mo/CIGS/CdS/AZO architecture.

A technological process for the low-cost production (design and manufacturing) of copper (Cu) based masks for evaporation of the required metal patterns, with different geometries, has been developed. This technological process was developed in order to have immediate feedback between the implementation and the original design. This allows to obtain masks for the evaporation of back contact for CIGS solar cells based on a low-cost, reproducible, controllable in terms of geometries and dimensions (also in the order of microns) process. The adopted protocol allows obtaining masks in a short time if compared to the time required by the electroerosion process. The procedure involves the use of a copper foil with a thickness of 0.1 mm on which the desired pattern, obtained by chemical etching using ferric chloride (FeCl<sub>3</sub>), is imprinted using the optical photolithography processes (Chapter 3 section 3).

It is widely reported in literature the use of acids for the production of patterns and printed circuits. The ferric chloride [1-2], is widely used both in industrial applications and in research activity, as it is one of the major etchant of copper due to both its high tolerance and low cost.

The ferric chloride hexahydrate  $FeCl_3 6H_2O_2$ , is one of the most used etchant acids, together with hydrochloric acid, HCl. At room temperature it comes up as a yellowbrown solid with a typical smell of chlorine, being also a harmful, irritating compound. FeCl<sub>3</sub> 6H<sub>2</sub>O has a solubility in water of 920 g / 1 at (20 ° C). However, in the methodology developed for the production of copper masks, a commercial solution with 45% by weight content of FeCl<sub>3</sub> has been used. This etchant solution shows a high tolerance to attack and dissolve copper and other metals. The chemistry, as well as the kinetics of dissolution of copper in a solution of ferric chloride is quite complex. Several ions and complexes are contained in this solution, such as Fe<sup>3+,</sup>  $FeCl_2^+$ ,  $FeCl_3$  and  $FeCl_4^-$ . Without entering into details, the chemical species are predominant in the chemical kinetics of the attack whenever concentrations of  $\text{FeCl}_2^+$ and FeCl<sub>3</sub> are increased. From the experimental point of view the formation constants K of cuprate complexes in solution, as well as the stability thermal constant  $\beta$  are important, because they affect the balance of formation and the saturability of the ferric chloride solution. The chemical action of the solution drops over time, since the presence of Cu<sup>2+</sup> ions tend to saturate the solution. This obviously entails a longer time of etching, causing also a lower resolution for the masks. The temperature of the bath solution represents another important factor. Experimentally it has been observed that the etching rate tends to increase with temperature (Figure 6.2).



Figure 6.1 : Calculated etching rate [1].



Figure 6.2: Temperature effect on etching rate [1].



Figure 6.3: Effect of FeCl<sub>3</sub> concentration Vs temperature on etching rate [1].

#### 6.1.2 Wet chemical etching

Wet chemical etching is a purely chemical process which consists of three steps: (1) the reactive species in a moderately strong Lewis acid solution attack the surface, (2) so a reaction in which soluble products are generated takes place (where the reaction can vary with the concentration of the acidic solution, determining then different attack rates) and, finally, such products are removed from the surface due to a diffusion mechanism depending on the dissolution kinetic constants and on the degree of saturation of the acid solution (3).



Figure 6.4 : Wet etching steps mechanism.

The wet etching considers some characteristic parameters: uniformity (transfer on the wafer of an ideal pattern, identical to that drawn on the mask; measurement of the eventual difference from ideality); Etching rate (amount of material removed in the time unit measured in nm / sec,  $\mu$ m / sec or Å / sec depending on the strength of the attack); Anisotropy (different etching rates in different directions);Selectivity (etching rates different for different compounds). Two important aspects in the context of a chemical excavation process are the selectivity and the directionality. The selectivity represents the capability of the etchant agent (FeCI3) in distinguishing between the masking layer and the layer to be excavated. In an isotropic excavation, the agent attacks the material in any direction, with the same speed, creating a semicircular profile beneath the mask (undercut). In an anisotropic etching, the dissolution rate depends on the specific directions and may result in straight walls or other non-circular profiles



Figure 6.5 Isotropic (a) and anisotropic (b) etching profiles.

A considerable advantage of the wet etching is the large number of existing and adaptable recipes, together with the possibility of varying more parameters of attack. The damage to the surface, however, is relatively low. Using well defined concentrations it is possible to have a constant attack speed, uniform even on relatively large areas. The disadvantages are the use of toxic chemicals and disposal as special waste.

## 6.1.3 Copper Mask realization

The technological process for the realization of mechanical masks consists in several steps in series, starting from the copper surface preparation, passing through the deposition of photoresist and the development of the desired photomask, up to the formation of the mask through chemical etching. The experimental recipe, widely reproducible, for the wet chemical etching in FeCl<sub>3</sub> is described below.

In order to obtain a drawing as faithful as possible to the copper mask, a series of parameters are optimized in order to obtain a chemical attack the more anisotropic it is possible. the experimental set-up and considered parameters are shown below.



Figure 6.6: Etching copper mask set-up.

- FeCl<sub>3</sub> solution at different concentration
- Temperature
- Etching time

- Complete copper foil immersion
- FeCl<sub>3</sub>solution agitation

It was noted that the best attack, about 150  $\mu$ m / 2h was obtained using a fresh solution of FeCl<sub>3</sub>, 45% in weight. For kinetic problems, the solution of ferric chloride over time tends to become saturated with copper ions, thus loses its power of attack. In the literature several recipes have been described, suggesting to increase dilutions or to integrate the solution with hydrochloric acid. Experimental tests have led to discard these configurations, because the attack is much less effective and above anisotropic with the addition of hydrochloric acid. In addition with mixed solutions of acids, the copper surface is very irregular and more ruined, so that the profiles of excavation show uneven walls. The volume of the solution represents another parameter that has been taken into account. The optimized volume has been found to be 100 ml, which seems a good compromise between a massive use of ferric chloride and the kinetics of a still competitive attack. Temperature is another fundamental factor. It has been amply demonstrated in the literature that the increase in temperature leads to an increase etch rate. The higher etching rate is obtained between 30 ° C and 40 ° C. At room temperature the strength of the ferric chloride solution is less efficient. At room temperature the strength of the ferric chloride solution is less efficient. At higher temperatures, not only there in no significant increase in the etch rate, but this process could also generate technical disadvantages consisting in the sealing of the polycarbonate, occurring at temperatures above 50  $^\circ$ C. The agitation and the orientation of the sample within the solution both play an important role in the etching process. Initially tests were carried out by immersing the sample the photomask side at the top in the solution and stirring it. The agitation from one side favors the removal of the surface oxide formation due to the attack through a concentric movement, but this advantage was lost positioning the specimen with the surface to be etched facing upwards. Following some cues taken from literature, it was decided to change configuration positioning the specimen with the surface which one would to etch facing downwards. In this way a better balance and a better kinetic of attack is obtained, as the etched copper does not tend to remain in contact with the excavation and behave as a passivating layer. The parameters of attack were experimentally defined in the following way. An initially cold FeCl3 solution, 45% weight, has been thermostated at 35 ° C. The sample has been positioned with the face of the photoresist developed downwards inside of a beaker with 100ml of not stirred solution. Attack times were precisely defined; in particular excavations loops of copper plates with a thickness of 0.2 mm has required times varying from 1h30 min to 2 h. The mask for the deposition of front contact on solar cells based on CIGS was manufactured starting from a copper (1 0 0) foil, 0.2 mm thick. On the foil some square areas (size  $55x55 \text{ cm}^2$ ) were cut. The steps carried out to manufacture such mask follow. Initially a chemical cleaning of the samples, performed strictly under the hood and wearing personal protection equipment (gloves, gowns, goggles), is carried out by rinsing the sample with:

- a) Hot trichloroethylene 100 ml;
- b) Hot Acetone 100ml;
- c) Hot Isopropyl Alcohol 100ml.

The first three steps have the physical task to degrease and clean the surface, eliminating carefully all possible traces of solvent through a drying in nitrogen flow. Then, a process aimed to even out the surface follows:

- d) mechanical polishing of the surface with sandpaper;
- e) chemical cleaning with HNO<sub>3</sub> 37 % solution for 5 min.

The surface preparation involves the removal of the surface sheet of copper oxide through the reaction:

$$3Cu + 8 HNO_3 \rightarrow 3 Cu (NO_3)_2 + 4 H_2O + 2NO$$
 (6.1)

It is worth to note that the copper undergoes a chemical attack by the nitric acid too, so it is not recommended to extend too much the attack time in order to avoid deep attacks.

f) rinsing with distilled water.

After this process, the sample is put in distilled water for further removal of possible residues. Then it is washed in a NaHCO<sub>3</sub>solution. On the surface of copper traces of nitric acid could remain. This might give rise some problems of stability in the deposition of the PR, especially during the phase in the oven at 90 ° C required for stabilizing the PR. Therefore the copper sheet is immersed in 1M solution of NaHCO<sub>3</sub>, acting as a buffer solution aimed to chemically neutralize the action of the remaining acid. Again, a rinse in distilled water is needed to remove traces of NaHCO<sub>3</sub>. After these chemical treatments, the preparation of the copper piece for rendering its surface the more homogeneous and clean it is possible has been considered. This step is aimed to act especially on copper oxide, as copper oxide strongly influence the deposition of the PR. For this reason, the samples are retracted again in organic solvents as follows:

- h) Rinsing in hot water 80 °C;
- i) Rinsing in hot acetone;

j) drying in nitrogen flux. The copper at this point is ready for optical photolithographic procedures. The drawings of the desired masks were obtained through Freehand software in 1:1 scale. Subsequently, the pads were printed on transparencies with printers ink jet at high resolution.





Two geometries have been used (fork and circular dots) for optical photolithography A photoresist layer, Microposit S1813, photosensitive to UV radiation, has been deposited on the copper foil. The PR deposition steps are summarized in the figure () below.



Figure 6.7: Photolitography steps.

The positive working photoresist S 1813 has been deposited by spin coating on the copper substrate. This is a photosensitive polymeric material which can be deposited in liquid form. The spin coating parameters allowing to obtain a thickness of 1.3 micron, representing an optimal thickness for an efficient development, are: spin coating speed 4000 rpm per min for a time of 30 seconds. After the photoresist deposition, the substrate is baked in an oven at 90  $^{\circ}$  C for 1 hour to remove the organic solvents in the resist and improve its adhesion to the underlying layer. Then the mask is aligned with the copper and exposed to the UV source. Finally the area exposed to UV radiation will then be removed with a developing bath. The design transferred in the resist is the positive of the mask.

#### 6.2 Front contact solar cell deposition

Minimized optical losses in the window layer require a reduction of its thickness. On the other hand, a good conductivity is required in order to avoid resistive current losses. A good trade-off can be achieved when the current collection is supported by a metal grid deposited onto the front contact. Although the application of the grid is beneficial to the cell performance, it also contributes to the reduction of the active cell area.



Figure 6.8 Device structure of a typical thin-film substrate solar cell.

Generally in CIGS solar cells with Al:ZnO window layer, Ni-Al grids are the most commonly used. A 50nm Ni layer is applied to reduce the formation of a resistive  $Al_{2}O_{3}$  barrier followed by a 1 µm thick Al layer [3]. These layers are typically deposited by electron-beam evaporation with shadow masks. This process has not been optimized yet. Further study is required in order to find the optimal front contact manufacturing conditions.

Mechanical masks have been fabricated both for 2-fingers devices (device 1, area=0.5 cm<sup>2</sup>) and circular dots (device 2, area=0.1 cm<sup>2</sup>).





Figure 6.9: Front contact specifications: (a) 2-finger (area=0.5 cm<sup>2</sup>) and (b) circular dots(area=0,1 cm<sup>2</sup>).

These masks have been used to deposit front Al contacts by e-gun, with a thickness of ~400 nm.

Initially, the fork mask, widely used in literature, have been used. In order to minimize the effect of defects, the circular dots have replaced the fork like contacts, as the area of the former contacts is wider.

#### **6.2.1.** Contact resistance measurements.

Contact resistance measurements have been performed using the TLM method in order to check the quality of the deposited contacts, carried out by comparing the evaluated parameters with literature data.

I-V curves have been recorded on couples of linear contacts defining different channel lengths (Figure 6.10) The Resistance values, calculated using Ohm's law from the measured I-V curves, have been plotted as a function of the contact distance, as reported in (Figure 6.11). From the best fit of the experimental data, using the expression (3.5) both sheet and contact resistance values have been assessed and reported in table Y.



Figure 6.10: TLM realized on TCO solar cell with Al contact.



Figure 6.11: Characteristics plot of the total resistance as a function of the contact separation in TLM structure.

Rc (Ω)	0.98
Rc (Ω/square)	11.2
Rsh (Ω/square)	1547
ρ (Ω/cm)	4x10 <sup>-2</sup>
N (cm <sup>-3</sup> )	10 <sup>19</sup>
$\mu$ (cm <sup>2</sup> /V s)	7

Table 6.1: Contact resistance of contact Al on TCO layer used in CIGS-based solar cells.

The agreement with literature data indicates the good quality of the electrical contacts. It is worth to note that the contact resistance value expected for circular shaped dots would be 0,19  $\Omega$ . Such value has been calculated by downscaling the result in table Y with respect to active area of the dots (0,018 cm<sup>2</sup>).

#### **6.3 Mechanical scriber for test device**

The monolithic integration into modules represents a special feature of the thin-film PV technology, since it would be desirable to eliminate some industrial steps required for the panels manufacturing. But, several aspect have to be kept under control for the manufacturing of efficient modules. In particular, connections between adjacent cells are formed during the material deposition, generating some undesirable drawbacks such as short-circuiting of adjacent cells or shunting between front and back contacts, due to cross talking and bad isolation of both back and front contacts.

The implementation of solar cells into modules requires the scribing of insulating patterns for the isolation of back and front contacts (required to avoid shunting phenomena) and the interconnection between cells (without short-circuiting them) forming the array.

Scribing process is generally carried out by means of a laser and/or mechanical tools. In particular, the insulating patterns on the back contact are obtained using an infrared YAG-laser (1064 nm). In this thesis work the scribing has been performed mechanically by using a tool, that is a blade. The SEM images of the scribing process applied to a CIGS based cell is reported in (Figure 6.12 a,b). Some straight lines corresponding to the back contact insulating patterns are visible in the central region of the pictures. A magnification of these lines, reported in (Figure 6.12 c), shows the efficiency the mechanical scribing of back contacts. The insulation between the back and front contact has been checked by means of Electron Beam Induced Current (EBIC) technique. EBIC is generally used to identify buried junctions or defects in semiconductors. It exploits the generation of an electric current scanning across the sample by means of energetic electrons. This EBIC current is influenced by the presence of various inhomogeneities, so, if used as imaging signal, allows to map in terms of bright contrasts the electron activity inside the sample. In (Figure 6.12 d) it is evident the lacking of shunts as the contrast of the active cell differs from the one

arising from the pattern. By comparison, SEM images collected at Helmotz Berlin Zentrum (HBZ), reported in (Figure 6.12 e,f) shows that the mechanical scribing of Mo contact is equally efficient and reproducible.



Figure 6.12 : SEM images of the scribing process: (a) (b) (c) thesis work, (d) EBIC images, (e) (f) HBZ scribing process.

#### **6.4 CIGS surface treatments.**

The fabrication of CIGS based solar cells requires a series of complex deposition steps and chemical treatments (cleaning and etching) on all surfaces composing the device. Chemical treatments on surfaces are aimed to guarantee their right chemical and, above all, physical properties for a better control of interfacial properties of both substrate/metal contact/photoreactive layers and heterojunction device CIGS/buffer layer/ZnO. In particular, CIGS film deposition results in layers generally showing a high roughness, with bumps as high as many hundreeds nm. From an operating point of view, a reduced roughness corresponds to a reduced active interface area and a lowering of dark current is expected too, due to an increase of  $V_{oc}$  (as large as 60mV) [4]. Literature shows some examples of chemical etching on CIGS surface using several bare etchants such as KCN, Br<sub>2</sub>, HCl or mixtures of etchants such as HCl:HNO<sub>3</sub>, NaOH:H<sub>2</sub>O2 and so on [5] [6].

In this thesis work, the attack efficiency of four different etchants have been preliminary tested on CIGS films deposited by PED technique (growth at 200 °C, 300 °C and 400 °C and showing the presence of about 400 nm height bumps) and classified on the basis of their strength, then the best one has been studied in detail in terms of both the attack time and the resulting film morphology.

Α	NaOH 1M + NaS <sub>2</sub> O <sub>3</sub> 0,5 M 1:1 30 s
В	KOH 1M +H <sub>2</sub> O <sub>2</sub> 10 ml 30 s
С	HCl + HNO <sub>3</sub> 1:2 30 s
D	Br <sub>2</sub> 0,2M + KBr 0,1 M 1:1 30 s

Table 6.2. Different wet chemical etching testate on CIGS film deposited by PED technique.

Table 6.2 summarizes the specifications of the tested etchant species (composition, concentration and attack time). The etch rate of the etching is showed in Figure 6.13, where a plot of the etched film thickness (reported as step height) as a function of the etching time for three etchant species, that is  $Br_2+KBr$ ,  $HCl+HNO_3$  and  $NaOH+NaS_2O_3$ , is reported.



Figure 6.13: Etch rate of different etchant species testated.

Clearly, the third species indicated above does not produce any substantial etching on CIGS films.

To better enlighten the effect of the chemical attack, SEM images of etched CIGS films (etching attack 250 sec) growth at 200, 300 and 400 °C, are reported in Figure 6.14.

# 1) CIGS grown at 200°C



(a) (b) (c) (d)

2) CIGS grown at 300°C



(c)

(d)

3) CIGS grown at 400°C



Figure 6.14: SEM images of CIGS film deposited at different temperature. The letter indicating different chemical etching used.

The letter indicating each image in (Figure 6.14) corresponds to the related species listed in (Table 6.2).

Images collected of CIGS films growth at 200 °C clearly evidence that species A

And B do not produce any relevant reduction of CIGS roughness, as the 400 nm height bumps are still present upon chemical etching. On the contrary, species C and D are suitable for an efficient etching. In particular, the species  $Br^- + KBr$  (Fig 6.14 D) turns out to be the most efficient one, as the bumps completely disappear upon treatment. It is worth to note that the surface chemical attack by species C and D is still actively efficient on films grown at 300 and 400 °C (second and third rows in Figure 6.14.

The etching mechanism corresponding to the species D can be described by a two steps reaction:

$$Cu\{In,Ga\}Se_{2} + \frac{5}{2}Br_{2} \longrightarrow \{Cu(II),Ga(III)\} + 2Se^{0} + 5Br^{-}$$
(6.2)  
$$Se^{0} + 2Br_{2} \rightarrow Se(IV) + 4Br^{-}$$

The high efficiency of such reaction has led to study the dynamics of the chemical attack. In this respect, AFM images reported in (Figure 6.14) for CIGS grown at 200 °C in functon of the etching time, show the expected correlation between the efficiency of the etching mechanism and the attack time, being clear from the CIGS film topography that the surface results to be well levelled after one minute of treatment.



Figure 6.15: AFM images of CIGS roughness surface with Br<sub>2</sub> + KBr etching treatment.



Figure 6.16: Etching time Br2 + KBr vs CIGS step heigth and RMS.

The above results are better displayed by performing a roughness (RMS, root mean square) and thickness (step height) qualitative analysis of the above morphological time evolution, as depicted in (Figure 6.16) where RMS and step height are reported in fuction of the etching time over a time scale of one minute. Clearly, the reduced roughness corresponds to a considerable reduced thickness too.

# References

- [1] Feng-Yuan Zhang J. Micromech Microeng. 16 8 (2006) N23-N27
- [2] C. Bryce Ind.Eng.Chem.Res. 34 (1995) 1412-1418.
- [3] A. Romeo et al., Prog. Photovolt: Res. Appl. (2004); 12:93-111
- [4] Canava et al., J phys chem of solids 64
- [5] T.Delsol et al, Solar energy materials &solar cells 77 (2003) 331-339.
- [6] B.Canava et al. Phys stat sol c 8 (2006) 2551-2554

## 7 CIGS solar cells characterization

After the optimization of the Mo deposition on SLG, the fabrication of the top ohmic contact and the procedures to define the area of the cell have been set up. The top ohmic contact has been realized by deposition in vacuum of Al, while mesa diodes have been defined by mechanical scriber. Laboratory small-area cell the performance, lifetime and reliability of which depend strongly on structural and processing-induced defects. These defects may be sites of excessive recombination, like grain boundaries or dislocations, or shunts being characterized by an increase of the local dark current. While recombination defects mainly degrade the short circuit current  $I_{SC}$  of the cells, shunts mainly degrade the fill factor FF and the open circuit voltage  $V_{OC}$  [1].

Then the complete cells have been characterized mainly by electrical techniques, such as current-voltage (I-V) in the dark and under illumination, infrared thermography and capacitance vs voltage measurements. This characterization was aimed at obtaining high efficiency CIGS-based cells through the optimization of the growth parameters and the free carrier density of the different layers. Hereinafter the main steps of the research activity, which allows situ reach efficiency of 15.5% on CIGS-based solar cells completely prepared at IMEM Institute, will be reported[2].

#### 7.1 CIGS-based solar cells finished to Bicocca and HBZ

The first complete solar cells on CIGS layer prepared by PED on Mo/SLG at IMEM were fabricated at the Helmholtz-Zentrum Berlin Institute (HBZ) and at the Bicocca University of Milan by the deposition of the buffer layer, the TCO layer and the top ohmic contact. The CIGS layer was nominally undoped and grown at a temperature of 450 °C. The buffer and TCO layers were those normally used to obtain CIGS-based solar cells in these Institutes which have a great experience in this field. In particular the buffer layer prepared at the HBZ Institute is formed by a thin film of In<sub>2</sub>S<sub>3</sub> grown using the Spray-ILGAR [3], while that prepared at the Bicocca is a CdS layer (70 nm) deposited by chemical bath deposition (CBD). As for the TCO in both cases is formed by a ZnO-Al:ZnO( 50nm -550 nm) layer grown by sputtering RF. The grid top contac is formed by a Ni-Al and no anti-reflective coating is used. (Figure 7.1) shows the IV characteristics under illumination of two typical cells prepared in the respective Institutes while (Table 7.1) reports the characteristic cell parameters.



Figure 7.1: Electrical characteristics under solar simulator (1.5 AM, 100mW/cm<sup>2</sup>) of the solar cells fabricated in the HBZ and Bicocca laboratories on CIGS/Mo/SLG prepared at IMEM.

Cells	Voc (V)	Jsc (mA/cm <sup>2</sup> )	Area (cm²)	FF (%)	Efficiency (%)
А	490	26	0.50	52	6.7
В	453	30	0.15	49	6.8

Table 7.1: Photovoltaic parameters of CIGS based solar cells fabricated in the HBZ and Bicocca laboratories on CIGS/Mo/SLG prepared at IMEM

From the figure 7.1 and table 7.1 it is possible to observe that the efficiencies of the cells are around 6.7-6.8% with comparable values of  $V_{oc}$  and  $I_{sc}$ . This result suggested that the CIGS layer and the CIGS/Mo/SLG structure prepared at IMEM were suitable for the preparation of CIGS based solar cells. C-V measurements, carried out at 300 K and with an high test frequency to avoid the contribution of deep levels, give a value of free carrier density around  $1 \times 10^{16}$  cm<sup>3</sup>, which is not to far from the doping level reported for high efficiency CIGS-based solar cells[4]



Figure 7.2: I-V characteristics in the dark and under solar simulator 1.5 AM of the HBZ (A) and Bicocca (B) cells respectively.

In figure 7.2 the I-V characteristics in the dark and under solar simulator 1.5 AM of HBZ (A) and Bicocca (B) cells respectively are reported.

The above structures have been characterized by infrared termography technique, to investigate possible shunting regions. Indeed, even thought a lot of effort is put into reducing shunts in photovoltaic devices, it is still common that manufactured and modules have shunts [5]. By IR thermography, as it has been previously reported [5-6-], it is possible to detect shunts in a non-destructive way.

Figure 7.3 shows the infrared thermography of HBZ (A) and Bicocca (B) solar cells respectively. It is evident that the HBZ cell shows two clear circular shunts through the structure, while the Bicocca cell exhibits an higher heating near the electric contact without the presence of shunts.



Figure 7.3: Infrared thermography images of HBZ (A) and Bicocca (B) cells respectively under forward bias of 1.5 V (HBZ) and 1.2 V (Bicocca).

The observed differences between the two images could be tentatively attributed to:

i) to the different buffer layers used in the two structures (  $In_2S_3$  in HBZ and CdS in Bicocca).

ii) different characteristics of the two CIGS layers employed in the HBZ and Bicocca cells and their different exposition to air before the buffer deposition

#### 7.2 CIGS-based solar cell with ZnS buffer layer prepared by PED

In order to prepare the whole CIGS solar cells by PED, as required in the "Industria 2015" project, the CdS buffer layer, usually prepared by CBD technique, has been replaced by a ZnS buffer layer grown by PED. The purpose was twofold:

- i) to obtaine Cd-free solar cells for environmental pollution reasons
- ii) to prepare structure in the PED system, so that the deposition processes of the different layers could be performed without breaking the vacuum, thus reducing process complexity and costs.

Several papers studied the deposition conditions by PLD (pulsed layer deposition) of ZnSe [7] and ZnS [8]. Due to the PED and PLD similarities, it can be deduced from the literature that the experimental conditions for growing ZnS and ZnSe layers are compatible with the electron gun working conditions. As a conclusion these layers should be easily deposited by PED. Taking into account that the "cadmium-free" ( with ZnS buffer ) photovoltaic cell performance has been found to be substantially comparable with that of cells containing CdS buffer layers, with maximum efficiencies very close to the threshold of 19% [9] Al:ZnO/ZnS/CIGS/Mo/SLG all PED structures have been prepared with the multilayer structure shown in Figure 7.4



Figure 7.4: Representative scheme of the all PED solar cell Al:ZnO/ZnS/CIGS/Mo/SLG prepared at IMEM.



Figure 7.5: Electrical characteristics of all PED Al:ZnO /ZnS (100nm)/CIGS/Mo/SLG prepared at IMEM under solar simulator (1.5 AM 100 mW/cm<sup>2</sup>).

Figure 7.5 shows the J-V caracteristics of the all PED Al:ZnO /ZnS/CIGS/Mo/SLG solar cells structure. It can be observed that the Voc value (475 mV) is relatively good but the Jsc ( $3 \text{ mA/cm}^2$ ) and the FF (0.32) are very low. The low FF could be associeted to an high series resistence as observed from the dark I-V characteristics of the sample (Figure 7.6).


Figure 7.6: I-V characteristics in the dark of all PED Al:ZnO /ZnS (100nm)/CIGS/Mo/SLG prepared at IMEM  $\cdot$ 



Figure 7.7: I-V characteristics of an all PED cells after annealing at different temperatures for 1 hour. In figure 7.5 are reported the I-V characteristics under solar simulator of an all PED Cd-free cell which has been annealed at different temperatures for 1 hour the

inspection of the figure it is evident that	Voc and Jsc increase with temperature up to
150°C, then decreasing at 200°C.	

Sample	As grown	T ann 120°C	T ann 150°C	T ann 200°C
Cell All PED	Voc = 215mV	Voc = 293mV	Voc = 317mV	Voc = 223mV
	Isc= 0.110mA	Isc= 0.139mA	Isc= 0.144mA	Isc= 0.103mA

Table 7.2: electrical parameters (Voc and Isc ) variation after annealing treatments .



Figure 7.8: Infrared thermography image all PED Al:ZnO /ZnS/CIGS/Mo/SLG prepared at IMEM  $\,$  under a forward bias of 1.5 V  $\,$ 

The infrared termography image, reported in figure 7.8, shows the presence of different circular shunts that could be responsible of the high dark reverse current and of the low short circuit current.

In conclusion the growth of Cd-free CIGS-based solar cells with ZnS buffer gave low efficiencies of the about 2-3 %. The reasons of this low performances could be attributed to:

- i) presence of shunts detected by infrared thermography
- ii) low doping levels of the CIGS absorbers, as revealed by by C-V measurements on twin CIGS/Mo/SLG samples grown simultaneously with those used to fabricate the cell.

Better photovoltaic efficiencies could be obtained by the optimization of the doping level and defect content of the CIGS and of the growth conditions of the ZnS buffer layer in order to reduce interface state defects and shunt channels.

## 7.3 CIGS-based solar cell with CdS buffer layer

Together with the developement of the all PED cell with ZnS buffer layer, CIGSbased solar cells with CdS buffer layer, completely fabricated at the IMEM Institute (all IMEM cell), have been also prepared. Since the ZnO/CdS/CIGS/Mo structure is more consolidated and better established with respect to that of ZnO/ZnS/CIGS/Mo, it has been thought to optimize the characteristics of the CIGS layer and of the other cell components by starting from the structure with CdS. In the "all IMEM" cells the CdS has been grown by bath deposition (CBD) while the CIGS, nominally undoped, has been grown by PED at 450 °C. The best electrical characteristics of these series of samples, whose scheme is reported in Figure 7.9, are shown in Figure7.10 and Figure 7.11.



Figure 7.9: Representative scheme of the all PED solar cell Al:ZnO/CdS/CIGS/Mo/SLG prepared at IMEM.



Figure 7.10: Electrical characteristics of Al:ZnO /CdS/CIGS/Mo/SLG prepared at IMEM under solar simulator (1.5 AM, 100 mW/cm<sup>2</sup>).



Figure 7.11: I-V characteristics in the dark AM Al:ZnO /CdS/CIGS/Mo/SLG prepared at IMEM. Also in this case the electrical characteristic under illumination shows a low

efficiency (2.7%) and a low FF (34.3).



Figure 7.12: Infrared thermography image Al:ZnO /CdS/CIGS/Mo/SLG prepared at IMEM under a forward bias of 1.5 V  $\,$ 

Moreover the infrared thermography indicated the presence of different shunts while the I-V characteristics in the dark exhibited an high series resistance (Fig.7.11) which again could be responsible of the low FF. The origin of the high series resistance could be attributed to several factors such as a low free carrier concentration in the CIGS or an high defect density at the CIGS/CdS-buffer interface. Indeed the CV measurements show a junction capacitance independent of the reverse voltage, which suggests that the depletion region at 0 V is comparable with the CICS thickness so the free carrier density is lower than 10<sup>15</sup>/cm<sup>3</sup>. In summary the that ZnO/CdS/CIGS/Mo/SLG "all IMEM" structure, obtained by using CIGS (PED) nominally undoped and CdS buffer prepared by CBD, shows an efficiency lower than that of the cells prepared by HBZ and Bicocca, but it proves that the structure grown at IMEM is suitable for fabricating CIGS-based solar cells. However the improvements of the photovoltaic performances of these junctions required clearly a better optimization of the characteristics of the single layers (in particular of the the resistivity and defect content of CIGS absorber) and of the CdS/CIGS interface.



#### 7.4 CIGS-based solar cells with selenization treatments

Figure 7.13: Representative scheme of the solar cell Al:ZnO/CdS/CIGS/Mo/SLG prepared at IMEM with post growth selenization treatments of CIGS

It has been reported that the growth of CIGS at high temperatures induces a modification of the film composition near the surface with the creation of Se vacancies which can be compensated by oxygen during the sample exposure to air before the deposition of CdS. This involves a worsening of the CdS/CIGS interface with a consequent reduction of the device performances. To reduce the interface defects and compensate the loss of Se at the surface the CIGS is generally subjected to the so called "selenization" treatement. The quality of the readily deposited CIGS material can be largely improved by a selenization with simultaneous annealing. When Se is supplied in the gas phase (for example as H<sub>2</sub>Se or elemental Se) at high temperatures the Se will become incorporated into the film by absorption and subsequent diffusion. These interactions include formation of Cu-In-Ga intermetallic alloys, formation of intermediate metal-selenide binary compounds, and phase separation of various stoichiometric CIGS compounds [10]. Using the selenization

some groups have reported CIGS solar cells performance with Voc( 600 mV) and efficiency of 14 % [11]. In order to improve the CdS/CIGS interface, layers of CIGS deposited by PED at 450 °C two selenization processes (at 250°C for 4 hours and 450°C for 30 minutes, respectively) were used. (Figure 7.14) reports the electrical characteristics of Al:ZnO /CdS/CIGS/Mo/SLG cells that underwent the above selenization treatments.



Figure 7.14: Electrical characteristics of Al:ZnO /CdS/CIGS/Mo/SLG prepared at IMEM under solar simulator 1.5 AM (100 mW/cm<sup>2</sup>) at different selenization treatments

Cell	T Se (C°)	Voc (V)	Jsc (mA/cm <sup>2</sup> )	Area (cm²)	FF (%)	Efficiency (%)
А	250	370	17	0.23	45	3.72
В	450	250	5	0.18	40	0.61

Table 7.3: Photovoltaic parameters of Al:ZnO /CdS/CIGS/Mo/SLG cells related to selenization treatments carried out at different temperatures

The electrical characteristics under solar simulator 1.5 AM, show that the process of selenization at lower temperature (250°C) for longer times (4 hours) is more effective than that performed at 450°C for 30 minutes. However, the selenization step does not involve a significant improvement in cell performance.



Figure 7.15: Infrared thermography image Al:ZnO /CdS/CIGS/Mo/SLG prepared at IMEM under a forward bias of 1.5 V with selenization treatment CIGS post growth at 250°C for 4 hours (A) and at 450°C for 30 minutes (B).

Figure 7.15 shows the thermographs for 2 cells analyzed. In both images (A) and (B), it is observed a strong heating in the vicinity of the top contact. The cell treated at  $450^{\circ}$ C (Fig.7.15 B) shows a more homogeneous and extended heating with respect to the cell selenized at  $250^{\circ}$ C (Fig.7.15 A) image (A) to selenization ( $250^{\circ}$  C) and clearly indicates the presence of a larger shunting area in accordance with the electrical characteristics described above.



Figure 7.16: Electrical characteristics under solar simulator 1.5 AM (100 mW/cm<sup>2</sup>) of a Al:ZnO /CdS/CIGS/Mo/SLG cell treated with Se at 450°C before and after aging.

The aging of the cell B (Selenized at 450  $^{\circ}$  C), shows an increase in efficiency of up to 5% after 6 months at RT in ambient atmosphere. However, this effect was not found on other cells analyzed. The high irreproducibility does not allow us to consider aging as a possible solution for a systematic improvement of the photovoltaic performances cells.

The analysis of the cells obtained with selenized CIGS films showed that there were no particular improvements in performance of photovoltaic devices.

In conclusion the analysis of the samples subjected to selenization treatements indicated no reproducible improvements in the performance of ZnS/CdS/CIGS/Mo solar cells. Moreover, since the selenization process represents an undesired extra step from the point of view of industrial costs, its application appear not suitable for CIGS-based cells.

### 7.5 CIGS-based solar cells with Na doped CIGS

The control of the CIGS p-type doping is crucial to optimize the solar cell performances and it is now widely accepted that doping level is mainly controlled by Na concentration and diffussion profile [12]. The role of sodium has been widely discussed in literature, but the mechanism is not fully understood yet and different models have been proposed. The Na-induced increase in carrier concentration in CIGS has been suggested to be due to incorporation of Na onto In or Ga lattice sites, where it would directly act as an acceptor [13]. Rockett [14] instead proposed that: i) Na acts to improve solar cell performance primarily via grain boundaries, presumably through changes in their electronic properties (such as electrical passivation), and ii) Na increases atomic mobilities during CIGS growth due to incorporation of Na onto In or Ga lattice sites and at grain boundaries, thus increasing grain size and establishing the lowest energy surfaces (Se-terminated (112) surfaces).

An activity performed by the PED group at IMEM to lower the CIGS growth temperature pointed out that CIGS absorber can be successfully grown at 270°C, but Na diffusion from SLG through the Mo layer is limited at this low growth temperature. In these conditions CIGS can be doped by Na by co-evaporating Na compounds such Na<sub>2</sub>Se [15], Na<sub>2</sub>S [16], NaF [17] or metallic Na [18].

At IMEM the desidered doping profile of CIGS has been obtained through PED deposition at 80°C of a NaF layer on the Mo back contact before CIGS deposition, so that Na diffusion takes place during its growth.



Figure 7.17: Representative scheme of the solar cell Al:ZnO/CdS/CIGS/NaF/Mo/SLG prepared at IMEM with Selenization treatments post CIGS growth by PED.

The cell was completed by a CdS buffer layer deposited by CBD and Al:ZnO deposited by PED.



Figure 7.18: Electrical characteristics of Al:ZnO /CdS/CIGS/NaF/Mo/SLG prepared at IMEM under solar simulator 1.5 AM (100 mW/cm<sup>2</sup>).

The electrical characteristics in figure 7.18 showed a J-V characteristic under solar simulator (red curve) with a low Voc and significant shunting.



Figure 7.19: Infrared thermography image Al:ZnO /ZnS/CIGS/NaF/Mo/SLG prepared at IMEM under a forward bias of 1.5 V. (A) before removal of shunted area, (B) after removal of shunted area

IR thermography pointed out that in the cell area two shunting regions are present (Figure 7.19 A), which were removed by scribing (Figure 7.19 B). The J-V characteristic measured under solar simulator after this removal, (Figure 7.18, blue curve) shows a considerable improvement of the photovoltaic cell performances, as shown in Table 7.4

	Thermography and scribing	V <sub>oc</sub> (mV)	J <sub>sc</sub> (mA/cm <sup>2</sup> )	FF (%)	Efficiency (%)
А	Before	84	16.06	25.05	0.34
В	After	482	35.42	53.20	9.10

Table 7.4 Photovoltaic parameters of Al:ZnO /CdS/CIGS/NaF/Mo/SLG cells (a) As grown, (b) after removed shunts by mechanical scribing

It is worth noting the efficiency increases to 9%.

The Na doping of the CIGS, introduced for PED through a layer of NaF, allowed us to obtain a dramatic improvement of the cell performances, the main issue remaining the presence of shunt channels likely due to the TCO deposition process.

## 7.6 CIGS-based solar cells optimized

The TCO deposition process was modified to minimize shunting and cells were prepared with themultilayer structure shown in Fig.7.20:



Figure 7.20: Representative scheme of the solar cell Al:ZnO/CdS/CIGS/NaF/Mo/SLG prepared at IMEM with TCO layer optimized[2]

The free carrier density in the CIGS absorber layer has been evaluated by capacitance-voltage (C-V) measurements performed on the cell structure, which gave (yielded) the Al:ZnO/CdS/CIGS/NaF/Mo solar cell with the best efficiency. Figure 7.21 reports the C-V profile obtained at 120 K using an ac test signal with a frequency of 1 Mhz and an amplitude of 25 mV.



Figure 7.21: C-V profile obtained on an Al:ZnO/n-CdS/p-CIGS/NaF/Mo cell at 120 K; dc bias from +0.4 to - 1 V, ac voltage frequency=1 Mhz, ac voltage amplitude=25 mV.

The free carrier density in the CIGS absorber layer has been evaluated by capacitance-voltage (C-V) measurements performed on the cell structure, which gave (yielded) the Al:ZnO/CdS/CIGS/NaF/Mo solar cell with the best efficiency. (Figure 7.21) reports the C-V profile obtained at 120 K using an ac test signal with a frequency of 1 Mhz and an amplitude of 25 mV. As can be seen the profile shows the typical U-shaped form commonly reported in the literature [19-20-21] with a minimum corresponding to a depletion layer width of about 0.95  $\mu$ m. In the above conditions the net acceptor concentration N<sub>A</sub> corresponds, as suggested by Cwil et al. [19], to the minimum value of the C-V profile that, in the present case, is about  $5 \times 10^{15}$  cm<sup>-3</sup> (see figure 7.21). The apparent increase of the doping level of more than one order of magnitude toward the back contact (depletion layer width >1 $\mu$ m) could be attributed to the accumulation of static charge in deep acceptors present in concentrations much higher than the net shallow density N<sub>A</sub> [19].



Figure 7.22: Electrical characteristics of Al:ZnO /CdS/CIGS/NaF/Mo/SLG prepared at IMEM under solar simulator 1.5 AM (100 mW/cm<sup>2</sup>) with TCO layer optimized[2]

The (J–V) characteristics under solar simulator at standard test conditions (AM1.5AM at 25°C). Figure 7.22 shows the J-V characteristic of the best of our laboratory cells (red line) alongside with a reference device grown at the same temperature with no intentional Na doping (blue line). The comparison of the two curves highlights the dramatic improvement of the photovoltaic efficiency obtained by tuning and optimising thickness and growth conditions of the NaF layer.

Device	NaF layer	V <sub>oc</sub> (mV)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF (%)	Efficiency (%)
А	with	584	37.5	69.4	15.2
В	without	350	18.4	34.3	2.7

Table 7.5: Photovoltaic parameters of CIGS based solar cells fabricated at IMEM at Tsub<300 °C with (A) and without (B) NaF layer[2]

In Table 7.5 the relevant photovoltaic parameters of the best solar cell (A) are summarized It is worth noting that our typical  $J_{SC}$  values are comparable to the best CIGS cells reported in the literature [22-23]while the  $V_{OC}$  is smaller but comparable to the typical values obtained with Na-doped CIGS grown by single-stage thermal co-evaporation[24].



Figure 7.23: Infrared thermography image Al:ZnO /ZnS/CIGS/NaF/Mo/SLG with TCO layer optimized prepared at IMEM under a forward bias of 1.5 V

In Figure 7.23 the infrared thermography image obtained at a forward voltage of 1.5 V is reported. As a consequence of the optimization of the various layers it can be clearly observed that no shunt channel is detected while the efficiency reaches the 15.2%. In particular, by considering the relatively high obtained efficiency it could be suggested that the optimized TCO layer, deposited by technique PED, reaches a quality comparable to those deposited by RF sputtering.



Figure 7.24: Theorical I-V dark characteristics of two Al:ZnO /CdS/CIGS/NaF/Mo/SLG solar cells.

Theorical I-V dark of two optimized cells Al:ZnO/CdS/CIGS/NaF/Mo/SLG is showed in Figure 7.24. In the plot is possible to observe four contributes that will be modified the I-V characteristics of the ideal equivalent circuit:

- 1) V < 0.2  $V/R_{sh}$  High resistance shunting
- 2) 0.3 < V > 0.5 J<sub>0</sub>[e<sup>[q(V-RsI)/nKT]</sup>-1] Leakage n=1 High ideality factor (n~3.6)
- 3) V>0.7  $J_2[e^{[q(V-R_sI)/2KT]}-1]$  High injection n= 2( phenomenological trend that the origin is still not clear).
- 4) V > 0.8 Resistance series Rs

	η= 15.2%	η= 13.5%
R <sub>sh</sub>	4.58 x10 <sup>5</sup>	1.61x10 <sup>5</sup>
J <sub>o</sub>	5.79x10 <sup>-9</sup>	1.09x10 <sup>-6</sup>
n	3.63	3.71
J <sub>s</sub>	$1.04 \times 10^{-13}$	$7.12 \times 10^{-14}$
J <sub>2</sub>	1.33x10 <sup>-8</sup>	1.40x10 <sup>-8</sup>
R <sub>s</sub>	4.74	4.47

Table 7.6: Value of shunt resistance and series resistance extrapolated

In table 7.6 has been showed the value of shunt resistance and series resistance extrapolated on I-V dark curve for both CIGS solar cells analyzed.

# 7.7 Conclusion

In conclusion we have shown that laboratory scale solar cells based on CIGS grown with a single stage deposition technique (PED) at T sub < 300°C can be achieve efficiencies as large as 15%. This results is to compared to the best efficiencies obtained in literature using other CIGS technique deposition such as 18% achieved by single stage evaporation but a T sub > 550°C and having a large presence of Se over flux. We have developed a process steps for optimized of buffer layer and TCO layer deposited by PED. Electrical characterization combine with infrared thermography have proved to be fundamental for determining of the performance of photovoltaic cells made, providing information for the optimization of the various layers on CIGS based solar cells.

#### References

- Green M A 1992 Solar Cells, Operating Principles, Technology, and System Applications (Kensigton, NSW: University of New South Wales) ISBN 0 85823 580 3.
- [2] S.Rampino et al., Appl.Phys.Lett 101, 132107 (2012).
- [3] N. A. Allsop et al., Prog. Photovolt: Res. Appl. (2005); 13:607-616.
- [4] R.Caballero et al., Prog.Photovoltaics 14, 145 (2006)
- [5] S. Johnston et al. J. Vac. Sci. Technol. A 28, 665 (2010).
- [6] O. Breitenstein et al., Prog. Photovolt: Res. Appl. (2004); 12:529-538
- [7] Y.R. Ryu et al., Applied Surface Science, 127-129, 496 (1998).
- [8] Z.J. Xin, et al., Semiconductor Science and Technology, 14 (8), 695 (1999).
- [9] D. Hariskos et al., Thin solid films, 480-481, 99 (2005)
- [10] B.J Stanbery et al., Critical reviews in Solid State and Materials Science 27 (2) 73 (2002).
- [11] V. Alberts et al., Thin Solid Films (2004); 451-452: 207-211.
- [12] Prof. Dr. Roland Scheer1, Prof. Dr. Hans-Werner Schock Thin Film Technology.
- [13] D. W. Niles et al., J. Vac. Sci. Technol. A, vol. 15, pp. 3044–3049, (1997).
- [14] A. Rockett, Thin Solid Films, vol. 361-362, pp. 330-337, (2000).
- [15] . E. Granata and J. R. Sites, *Proceedings of the* 2nd *World Conference on Photovoltaic Solar Energy Conversion*, vol. I, pp. 604–607, 1998.],
- [16] T. Nakada, et al., *Proceedings of the 14th European Photovoltaic Solar Energy Conference*, vol. 2, pp. 2143–2146, (1997)
- [17] K. Granath, et al., Sol. Energy Mater. Sol. Cells, vol. 60, pp. 279–293, (2000).
- [18] M. Lammer et al., Thin Solid Films, vol. 387, pp. 33-36, (2001).
- [19] M. Cwil, et al., J. Appl. Phys. 103, 063701 (2008)
- [20] T. Eisenbarth, et al., Appl. Phys. 107, 034509 (2010)
- [21] M. Cwil, et al., Thin Solid Films 515, 6229 (2007)
- [22] P.Jackons et al., Prog.Photovoltaics 19, 894 (2011).

- [23] I.Repins et al., Prog.Photovoltaics 16 235 (2008).
- [24] M.Lammer et al., Thin Solid Films 387, 33 (2001).

# Conclusions

The present work has been mainly devoted to the preparation of the Mo layers on conventional SLG substrate and to both the study and the optimization of alternative substrates (ceramic and cement) for building integration. Solar cells technological realization processes (mechanical scribing and top Al ohmic contact deposition) was carried out. Electrical characterization of Al/ZnO/CdS/CIGS/Mo/SLG solar cell standard prototype, prepared at the IMEM institute and supported by the programme "Industria 2015" of the Italian Ministry of Economic Development (Grant EE01\_00662, "PED4PV), was performed.

At first, great efforts have been dedicated to the optimization of the growth parameters of Mo layers on SLG by sputtering and a procedure for substrates cleaning was studied, revealing to be fundamental in order to have a good adhesion of Mo electrical contact. We analyzed the deposition influence of sputtering parameters on Mo films properties. This contact, which represents the back ohmic contact in CIGS-based cells, has a considerable influence on the performance of the final device. Low contact resistances with the CIGS layers have been obtained upon sputtering optimization.

Drawbacks of alternative substrates (e.g vacuum compatibility, surface porosity and roughness) have been studied with the aim at obtaining a substrate compatible with the deposition of thin layers.

A mechanical scribing process has been developed for the realization of test device solar cells. Copper mechanical masks have been realized for deposition of front contacts. Then test structures of Al/CIGS/Mo (Schottky contact) and In/CdS(ZnS)BL/CIGS/Mo (ohmic contacts) have been prepared in order to obtain information about both the free carrier concentration in the CIGS layer and the electrical characteristics of the BL/CIGS junctions. The results gave useful suggestions to improve the characteristics of the prototype PV devices.

Finally, the finite solar cells Al/ZnO/CdS(ZnS)/CIGS/Mo/SLG have been fabricated by evaporating the Al top contact with desired geometry. These cells have been investigated by current-voltage measurements, in dark conditions and under illumination of a solar simulator, to determine the characteristics of photovoltaic devices, by capacitance-voltage technique to obtain information on the shallow and deep electronic levels in the CIGS layers after the deposition of the BL and ZnO layer and by infrared thermography to evidence possible shunt channels through the structures. The feedback between the results of the above characterizations with the growth parameters of the different layers forming the solar cells, allowed to optimize the device characteristics and to obtain, then, CIGS-based solar cells, prepared completely at the IMEM institute, with efficiency up to 15.2%.

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