UNIVERSITÀ DI PARMA

DIPARTIMENTO DI SCIENZE MATEMATICHE, FISICHE E INFORMATICHE

PhD IN PHYSICS

XXX CYCLE

FINAL REPORT

Candidate	Greta Rosa
Thesis title	Improvements in CdTe- and CIGS-based thin-film solar cells and investigation on new materials for photovoltaic applications.
Supervisor	Prof. Alessio Bosio
Coordinator	Prof. Cristiano Viappiani

DESCRIPTION OF RESEARCH ACTIVITIES AND EXPERIMENTAL RESULTS

RESEARCH AIMS

The aim of my PhD research was the performance improvement of CdTe- and $CuInGaSe_2$- based thin-film solar cells, which were completely produced in-house at the Thin-Film Laboratory (ThiFiLab) of the University of Parma. In particular, my work was focused on three main objectives:

1. Implementation of high-performance CdTe-based devices fabricated using close-spaced sublimation (CSS) and sputtering in an attempt to improve both grain boundary passivation and back-contact ohmicity.
2. Implementation of high-efficiency (> 16%) CIGS-based devices with the aim of exporting the fabrication process developed for soda-lime glass and ceramic substrates to flexible substrates, such as thin metal foils.
3. Investigation of sputter-deposited delafossite as a novel transparent conducting oxide (TCO) for photovoltaic (PV) and electronic applications.

INTRODUCTION

Currently, the technology of thin-film solar cells is one of the most promising for low-cost renewable energy production. CdTe- and CIGS-based cells, which achieved record efficiencies of 22.1% and 22.6%, respectively, are the most attractive among thin-film solar cells. These high efficiencies have had a huge influence in making them highly competitive in the photovoltaic market, with an estimated final cost per module lower than US $ 0.50 per peak-watt (W_p).

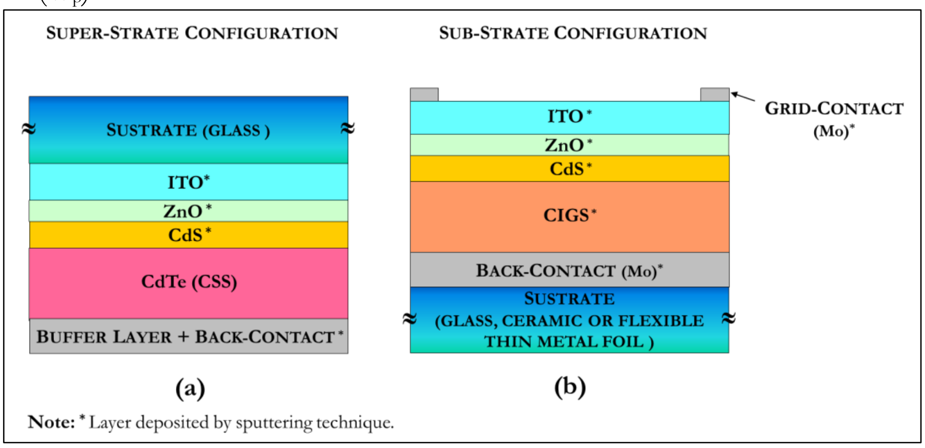

Figure 1 Structure of (a) a CdTe- and (b) a CIGS-based solar cell.

At ThiFiLab, a fully scalable process to produce both of these high-efficiency solar cells has been studied. The only techniques our process requires to produce these devices are: CSS and sputtering for CdTe cells and sputtering and selenisation for CIGS cells. Our choice of sputtering as a core deposition technique is justified by its great flexibility: it can be used to deposit a wide variety of materials, such as insulators, semiconductors, conductors, alloys and composites. At the same time, we have chosen to use CSS in making CdTe films because it is one of the simplest approaches to physical vapour deposition and it offers high deposition rates. The typical configuration we followed to produce our CdTe- and CIGS-based solar cells is reported in Figure 1.

RESEARCH WORK AND EXPERIMENTAL RESULTS

Research work is reported here in three separate parts, one for each stated objective:

1. **Polycrystalline CdTe-based solar cells**

We focused to improve two key aspects of CdTe-based cell operation: grain boundary passivation and back-contact ohmicity and stability.

Grain boundary passivation

CdTe layers are usually fabricated using CSS, a technique that can produce compact films only for thicknesses in the range of 6 ÷ 8 μm. Thicker absorber layers can sometimes be employed to avoid pinholes and recombination paths of charge carriers into grain boundaries. However, the thickness of CSS-deposited film is significantly higher than necessary. Because the band-gap energy (E_G) of CdTe is 1.45 eV and because its absorption coefficient in the visible part of the solar spectrum is quite high (> 10^4 cm^{-1}), 1 μm-thick layer of material would be enough to absorb about 90% of the incoming radiation. To assess the extent of this problem, an attempt was made to deposit a CdTe film of only about (3 ÷ 4) μm and the film was found to show cavities (Figure 2a). To correct this situation and fill these cavities, a second, (100 ÷ 200) nm-thick CdTe layer was sputtered on top of the first inhomogeneous CdTe film (Figure 2b). The resulting CdTe bi-layer was subsequently heat-treated at 670 K under a controlled chlorine atmosphere (Figure 2c) and the solar cell was completed with a Bi_2Te_3-Cu-Mo back-contact. It was observed that the film deposited by sputtering results to be an *n*-type layer (with a resistivity of about 10^6 Ωcm), compared to the CSS-deposited film that is a *p*-type layer.

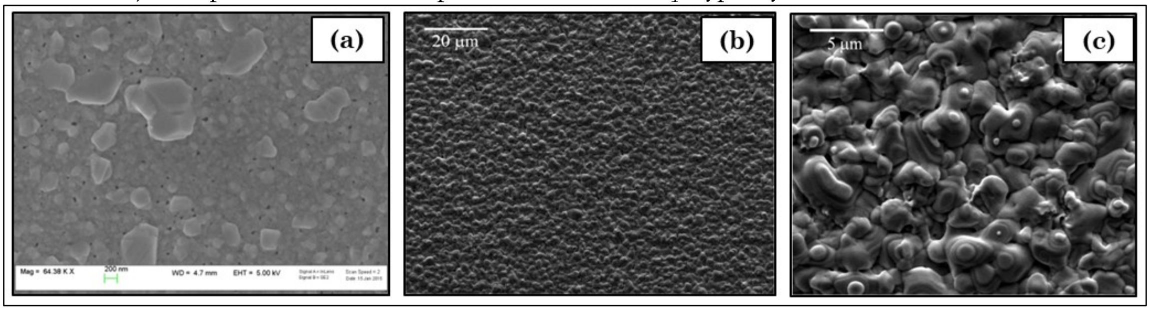

Figure 2 Morphology SEM images of: (a) 3 μm-thick CdTe film deposited using CSS, (b) 3 μm-thick CSS-deposited CdTe + 200 nm-thick sputtered CdTe, (c) the film (b) after a heat treatment at 670 K under a controlled chlorine atmosphere.

After the chlorine treatment, grain boundaries show a localized Cl segregation (*n*-type levels). This results in the formation of a *p*-*n*-*p* junction across each grain boundary. Thus, there is a built-in field in the region between the grain border and its interior, which acts as a mirror for the minority carriers and leads to an increase of their average lifetime.

Table 1 Comparison between the PV parameters of three CdTe-based solar cells. Note: * Series (R_S) and shunt (R_{Sh}) resistances, referred to solar cells with an area of 1 cm^2, have been extrapolated from the under-light J-V characteristics.

# Sample	V_{OC} (mV)	I_{SC} (mA)	FF (%)	η (%)	R_S* [Ohm]	R_{Sh}* [Ohm]
5333	830	25.2	70.0	14.94	5.6 ± 0.02	1428 ± 20
5591	860	26.1	59.2	13.19	10.6 ± 0.04	1250 ± 9
5561	786	24.5	50.4	9.36	14.2 ± 0.01	227 ± 5

In Table 1, a comparison between the PV parameters of various solar cells is reported. Sample #5333 is one produced using the method described above, while sample #5991 and sample #5561 are the result of a single CSS deposition of a 8 μm-thick and a 3 μm-thick CdTe layer, respectively. The new method for enhancing the electrical passivation of grain boundaries shows the best results.

Back-contact ohmicity and stability

A barrier-free back contact is fundamental to improve the efficiency of CdTe/CdS solar cells. Several attempts were made and different buffer materials such as As_2Te_3, Bi_2Te_3 and ZnTe were tested. Each buffer layer was covered with about 10 nm of copper deposited at a substrate temperature of 520 K. Each contact was finished by adding a thin layer of platinum (~10 nm) and then a thicker layer of molybdenum (~200 nm). Platinum is known for its high work function (5.8 eV) and this makes it a suitable material for ohmic contacts connecting *p*-type high-conductivity buffer layers. The results for As_2Te_3, Bi_2Te_3 and ZnTe are very similar and cell efficiencies are on the order of (15 ÷ 16)% with a fill factor of (0.7 ÷ 0.72). What makes a difference is the presence of platinum, which was confirmed to be fundamental. Figure 3 (which refers to a ZnTe back contact) shows that, when platinum is not used in the external contact, a roll-over appears in the J-V characteristic, causing a significant deviation from the high-voltage ideal profile.

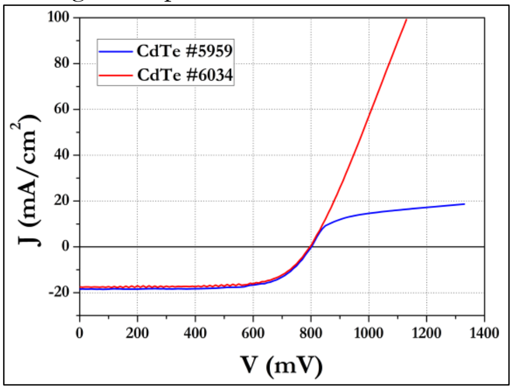

Figure 3 Comparison between sample CdTe #5959 (external contact is made without platinum) and sample CdTe #6034 (external contact is made with platinum). J-V characteristics were measured under the Standard Test Condition (STC) – namely, incident power density of 1000 W/m², a temperature of 298.15 K, under AM 1.5 filtered solar light spectrum.

2. Polycrystalline CIGS-based solar cells

Our standard process to prepare $Cu(In,Ga)Se_2$ precursors involves the use of three different sputtering targets: InSe, GaSe and Cu. Precursors are then selenised in Se-vapour. An investigation of the process requirements that must be met to obtain high-quality precursors on a soda-lime glass substrate and for creation of high-efficiency CIGS solar cells has led to the following conclusions:

- InSe and GaSe targets should have a density higher than 97% to avoid being damaged during the sputtering deposition.
- Sputtering power requires tuning, especially for InSe. We have found that the correct setting for sputtering power is about 3.8 W/cm². By setting this value, we were able to prevent both indium segregation on the target surface and the peeling effect of the film from substrate that occurs during selenisation when an incorrect (too low or high, respectively) sputtering power is used.
- The substrate temperature (T_S) must be carefully chosen, as well, especially for InSe. If the temperature of the substrate is higher than 670 K, the InSe film will contain an excess of In, whereas, if the temperature is lower than 470 K, it will contain an excess of Se.
- The deposition rate of Se during selenisation also plays an important role. It has been found that the average grain size of the finished $Cu(In,Ga)Se_2$ film is larger when the evaporation rate of Se is around 1 μm/s.

These results have been used to extend this process, standard for soda-lime glass and ceramic substrates, to flexible thin metal foil substrates. However, the obtained results have not met our expectations: measurements on the most promising sample yielded a V_{OC} of 540 mV, a J_{SC} of 22.09 mA/cm², an FF of 0.40% with an efficiency of only 6.2%. The reason why these values are lower to those commonly obtained with a glass/ceramic substrate is because this new type of substrate introduced new technological challenges, such as:

- A problem of film adhesion.
- The necessity of a barrier layer between the metallic substrates and the active layer in order to prevent the diffusion of impurities, such Fe, Ni, and Cr, and to provide electrical insulation between the metal substrate and the monolithically interconnected solar cells.
- The need of using optimised sputtering conditions; in particular, the substrate temperature.

3. **Delafossite as a new material for PV applications**

The copper-based delafossite family $CuMO_2$ (where M = B, Al, Ga, In, Fe, Co, Cr) represents the most promising materials for *p*-type TCO. We tried to sputter-deposit these materials to test their effectiveness as back contacts in bifacial CIGS solar cells and in CdTe cells (where they would replace the metal and buffer layer). Specifically, we tried polycrystalline thin-films of $CuGaO_2$ and $CuBO_2$. In the case of $CuGaO_2$, we used a sputtering target with a Cu/Ga ratio of 0.5 and the deposition was made in presence of oxygen as reactive gas. Unfortunately, we found out that an excessively high T_S (850 K) was required to deposit a thin film of $CuGaO_2$. $CuBO_2$ films were obtained using a two-stage deposition process: an electron beam assisted deposition of a B_2O_3 layer followed by sputtering deposition of a Cu film. Since B_2O_3 films can be treated as a glassy systems, we took advantage of the material softening point at about 720 K to perform the Cu deposition under quasi-rheotaxial conditions. An annealing treatment followed the deposition.
In both cases, the search for a method to dope these films with elements belonging to the second group of the periodic table of the elements in order to make them conductive is still currently under way.

CONCLUSION

At the end of my PhD course, I have been able to achieve several of my initial goals:

- The development of an innovative process, reducing the thickness of the CdTe absorber layer and incorporating a barrier-free back contact, suitable for the production of high-efficiency solar cells.
- The identification of the main requirements needed for preparing high-efficiency $CuInGaSe_2$-based solar cells making use of scalable techniques such as sputtering and selenisation.
- The successful sputtering-based preparation of $CuGaO_2$ and $CuBO_2$ delafossite thin films for use as transparent back contacts in bifacial CIGS- and CdTe-based solar cells.

TAUGHT COURSES

- Formazione Generale alla Prevenzione e alla Sicurezza sul Lavoro. (E-learning)
- Study Skills. (Prof. Anila Scott-Monkhouse)
- Simulazione multifisica con COMSOL. (Prof. Paolo Cova)
- Materiali e Dispositivi Fotovoltaici. (Prof. Alessio Bosio)
- How to survive after a PhD thesis. (Prof. David Karlin)
- Advanced Photonics. (Prof. Federica Poli)
- Impatto ambientale dei sistemi energetici. (Prof. Agostino Gambarotta)
- Academic Research Skills Training Course. (Prof. Stephen A. Quarrie)

ORIENTATION AND TRAINING ACTIVITIES

Tutor in the dissemination of scientific culture:

- Olimpiadi della Fisica;
- Laboratori di Nano-scienze;
- Seminario di Orientamento per studenti Laurea Triennale di Fisica;
- Alternanza Scuola - Lavoro;
- Alla scoperta del mestiere del Fisico;
- Notte dei Ricercatori 2015;
- Laboratori della Luce;
- Piano Lauree Scientifiche (PLS).

Assistant to the course exam 'Tecnologie Fisiche per Energia e Ambiente'.

PUBLICATION LIST

1. A. Bosio, N. Romeo, D. Menossi, **G. Rosa**, P.P. Lottici, A. Romeo, I. Rimmaudo and A. Salavei, 'Key Developments in CdTe Thin Film Solar Cell Back-Contact', Proceedings of 28TH European Photovoltaic Solar Energy Conference and Exhibition (EU-PVSEC), (2013), 2357 - 2361;

2. A. Bosio, D. Menossi, **G. Rosa** and N. Romeo, 'Key developments in CIGS thin film solar cells on ceramic substrates', *Crystal Research and Technology*, (2014), 49, 8, 620 – 627;
3. N. Romeo, A. Bosio, D. Menossi, **G. Rosa**, A. Salavei and A. Romeo, 'Improvement in Processing CdTe/CdS Thin Film Solar Cells', Proceedings of 29TH European Photovoltaic Solar Energy Conference and Exhibition (EU-PVSEC), (2014), 1709 – 1712;
4. A. Bosio, D. Menossi and **G. Rosa**, 'Il fotovoltaico di seconda generazione diventa competitivo', 1st ed., Publisher: Aracne Editrice, Italy, (2015);
5. A. Bosio, **G. Rosa**, D. Menossi and N. Romeo, 'Influence of Stoichiometry on Grain Boundary Passivation in Polycrystalline CdTe Thin Films', *Energies*, (2016), 9, 254;
6. **G. Rosa**, A. Bosio, D. Menossi and N. Romeo, 'How the Starting Precursor Influences the Properties of Polycrystalline $CuInGaSe_2$ Thin Films Prepared by Sputtering and Selenization', *Energies*, (2016), 9, 354;
7. A. Bosio, **G. Rosa**, S. Mazzamuto, A. Romeo and N. Romeo, 'The Influence of Compound Target Preparation, Sputtering Power and Substrate Temperature on the Achievement of $Cu(In,Ga)Se_2$ Precursors Suitable to Get High Efficiency Solar Cells', Proceedings of 32TH European Photovoltaic Solar Energy Conference and Exhibition (EU-PVSEC), (2016);
8. N. Romeo, **G. Rosa** and A. Bosio, 'The back contact in CdTe/CdS thin film solar cells', submitted to SWC 2017/SHC 2017 conference, (2017);
9. A. Bosio, **G. Rosa** and N. Romeo, 'Past, Present and Future of the Thin Film CdTe/CdS Solar Cells', Solar Energy - Special issue: 'Recent Progress in Photovoltaics, Part 1', to be submitted.

CONFERENCE AND WORKSHOP ATTENDANCE

- 1ST PARMA NANO-DAY (Parma, 28/11/2015)
- COMSOL Multiphysics 5.0 Workshop (Parma, 22/04/2015)
- EU PVSEC 2015 – 31TH European Photovoltaic Solar Energy Conference and Exhibition (Hamburg, 14 – 18 September 2015)
- EU PVSEC 2016 – 32TH European Photovoltaic Solar Energy Conference and Exhibition (Munich, 20 – 24 June 2016)
- E-MRS 2016 Fall – European Materials Research Society and Exhibition (Warsaw, 20 – 24 September 2016)

SEMINAR ATTENDANCE

- Atomic scale nanoelectronics: advancements and directions. (Enrico Prati)
- Advanced microscopies for characterization and nanofabrication. (M. Ricardo Ibarra)
- La fisica nella percezione del colore: storia e applicazioni. (Claudio Oleari)
- Discovery of quasicrystals in nature: Implications from condensed matter physics to the early stages of the Solar System. (Luca Bindi)
- Iron superconductors: high transition temperatures in molecular intercalates of FeSe. (Stephen J. Blundell)
- Didattica e Divulgazione della Scienza. (Marco Fabbrichesi)
- Ferromagnetic Nanoparticles: building blocks of future magnets. (J.P. Liu)
- Model Order Reduction Techniques for Control and Optimization of Automotive Energy Conversion and Storage Systems. (Marcello Canova)
- Optimization and Optimal Control of Energy Systems. (Stephanie Stockar)
- Development of high efficiency multi-junction solar cells. (Gianluca Timò)
- In-situ characterization and control of MBE growth of III-V nanostructures by means optical techniques at IMM. (Fernando Briones)
- Il premio Nobel 2016: la topologia, un investimento per il futuro della Fisica. (Prof. Laura Romanò)
- Creating world's tiniest machines. (Alberto Credi)
- Macedonio Melloni e le origini della sorveglianza dei vulcani.

(Giovanni Pasquale Ricciardi)

- Pulsed neutrons for materials research. (Felix Fernandez-Alonso)
- Astronomia nell'infrarosso: studiare le stufe cosmiche. (Daniele Gardiol)
- Analisi termografica a raggi infrarossi in edilizia. (Elena Lucchi)
