https://doi.org/10.1007/s00339-019-2874-4

Optoelectronic characterization of $CuInGa(S)_2$ thin films grown by Spray pyrolysis for photovoltaic application

Amal Bouich[1, 2,] Bouchaib Hartiti[3], Shafi Ullah[1], Hanif Ullah[1], Mohamed Ebn Touhami[2], D.M.F. Santos[4], Bernabé Mari[1]

Institut de Disseny i Fabricació, Universitat Politècnica de València. Camí de Vera s/n 46022 València, Spain[1]
LMEE laboratory, Faculty of Sciences, BP 133, Kenitra, Morocco[2]
MAC&PM Laboratory, ANEPMAER Group FSTM, B.P 146, Mohamedia, Morocco[3]
CeFEMA, IST-U Lisboa, Portugal[4]

Abstract

Copper-indium Gallium disulfide ($CuInGaS_2$) is a good absorber for photovoltaic application, Thin films (CIGS) were prepared by spray pyrolysis on glass substrates in the ambient atmosphere. The films were characterized by different technique, like structural, morphological, optical, and electrical properties of $CuInGaS_2$ films were analyzed by X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), spectrophotometer and Hall effect respectively. After optimization the deposited films structure, grain size and crystallinity became more important with an increase of annealing time at 370 °C for 20 min, Transmission electron microscopy (TEM) analysis reveled that the cable sheet are well crystalized and the inter planer distance are 0.25 nm, 0.28 nm and 0.36 nm. The Atomic Force Microscope (AFM) observation shows that the grain size and roughness can be tolerated by optimizing the annealing time. The strong absorbance and low transmittance were observed for the prepared films with a suitable energy band gap about 1.46 eV.

The Hall-effect measurement system revealed that CIGS films exhibited optimal electrical properties, resistivity, carrier mobility and carrier concentration were determined to be 4.22 $\times 10^6\ \Omega$ cm, 6.18$\times$ 10^2 $cm^2.V^{-1}.\ S^{-1}$ and 4.22 $\times$ 10^6 cm^{-3}, respectively. The optoelectronic properties of this material $CuInGaS_2$ makes it recommended to be used for the manufacture of solar panels more efficient.

Key words; Spray pyrolysis, annealing, XRD, SEM, AFM and Optical analysis.

2-Introduction:

Photovoltaic energy is a precious and effective energy. current research is oriented towards the manufacture of solar panels with a high conversion rate of light into electricity with a low cost [1] to have a very good performance of the photovoltaic cells it is necessary to improve the properties of the semiconductors which constitute the solar cells [2] for this reason, CIGS thin films are among the most widely used thin films due to their physical characteristics because its yield reaches up to 22.8% [3]. CIGS have a live bandgap only with the control of the substitution by Ga can be from 1.04 eV to 1.68 eV, and high optical absorption coefficient of 10^5 cm^{-1} [4].

Several techniques are developed to elaborate CIGS thin films such as sputtering [5], PVD[6], CVD[7], sol gel [8], Electrodeposition [9], co-evaporation [10], pulsed laser deposition[11], and spray pyrolysis as a technique has several advantages among them it is at the least cost, simple to implement and allow a large production area [12].

CIGS thin films were developed by spray pyrolysis in different annealing times and characterized by X-ray diffraction, The Atomic Force Microscope (AFM), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), UV- visible and with four probe method to get an idea of the structural characteristics, the morphology, and the optical and electrical properties of the thin layers. the annealing temperature has a great impact on the recanalization and the morphology also on the efficiency of the photovoltaic cell, which is why we have found the interest to make a complete study on the adequacy of this parameter on the CIGS thin films with different annealing times with the same annealing temperature which equals 370 °C.

3-Experimental:

1. The precursors used,

For the deposition of CIGS thin films, a solution has been prepared which contains different masses of the three precursors, $CuCl_2$, $InCl_3$, $SC(NH_2)_2$ or they are dissolved in distilled water after we have from the Gallium with a percentage of 10 percent of indium. we deposited the solution by the technique of spray pyrolysis on a cleaned glass substrate.

2. Deposition technique,

The deposition of the thin layer by spray pyrolysis is controlled by the spraying of the solution on a heated substrate which can be controlled by the setting of the spray rate by the Automator which a direct impact on the surface of the substrate is, the spraying time is related to the thickness of the deposited thin film [13]. The parameters of the pyrolysis spray technique which are bound to the technique have been fixed so that the temperature of the substrates is set at 370 °C. The pulverization rate has D = 1 ml / min, the distance between the atomizer and substrate is fixed d = 25cm, the spray time set half an hour. after the deposition of the thin layer it was treated with different time.

Spray technique involves preparing CIGS ($CuInGaS_2$) from electrolytic bath containing the Cu-In-Ga-S elements in the form $CuCl_2$, $InCl_3$, $GaCl_3$, $SC(NH_2)_2$, Thin layers were deposited on glass substrates at 370 °C using the spray pyrolysis technique [13]. CIGS thin films were prepared using different precursors, $CuCl_2$ (1.10^{-2} M), $InCl_3$ (1.10^{-2} M), $GaCl_2$ (1.10^{-2} M) and SC2 $(NH^2)^2$ (3.10^{-2} M) as a sulfur source which were dissolved in distilled water and the obtain a solution was sprayed in air on Preheated glass substrates of dimension (2cm x 2cm x 1mm) at 370°C temperature, using the spray rate of D = 1ml / min, the distance between the atomizer and the glass substrate is 25 cm and the spray time was set at t = 30 min.

During the spray all parameters were fixed, only annealing time were change throughout the deposition. Afterwards, the samples were rinsed under DI water and dried in 60 °C oven for 5 min. for the crystallinity improvement the as - deposited samples were annealed in a furnace tube at 370 ºC for different annealing time.

Table 1: the deposition conditions of sprayed CIGS

Samples name	Annealing temperature (°C)	Pression (bar)	Thickness (µm)	annealing time (min)
Sprayed CIGS 1	370	2.5	2	5
Sprayed CIGS 2	370	2.5	2	10
Sprayed CIGS 3	370	2.5	2	20

4-Results and Discussion:

X-ray diffraction measurements (XRD):

The obtained films have a crystalline structure similar to chalcopyrite. The spectra shows maximum intensity for peaks [112], [220-204] and [312-116], while the more intense [112] peak appears in all spectra indicating that growth is preferred in this direction [14] at the intensity level we analysis that the most intense peaks corresponding to the sample CIGS3 with 20 min of annealing time shows that the intensity increases with the annealing time.

lattice parameters:

To calculate the lattice parameters [15] could be used two equations 1 and 2 taking into consideration the following values: the angle 2θ and the value of the plan hkl correspondent:

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}. \quad (1)$$

https://doi.org/10.1007/s00339-019-2874-4

$$n\lambda = d_{hk_l}\sin(\theta) \quad (2)$$

a, c: lattice parameters, d $_{hkl}$ is the lattice spacing of hkl. h, k and l are the Miller indices, k is the wavelength of the CuK_α radiation (0.154 nm), 2θ is the diffraction angle of the corresponding plane. After the calculation we got the lattice parameters.

a= 5,54 Å and c= 11,14 Å

Grain size and effective lattice strain:

Effective lattice strain can give us an idea about the imperfections and deformations of the grains in the level of the thin layer sprayed, for the calculation we can use the following equation (3) where it links the grain size with the effective lattice strain [16]. The grain size of the films sprayed CIGS increased from 2.8 nm to 7.67 nm with increase of annealing time (Table 2).

$$\beta\cos(\theta) = \frac{k\lambda}{D} + 4\,\varepsilon\sin(\theta) \quad (3)$$

Where K is a constant whose value was taken as 0.94, k is the wavelength of X-ray used, β is the full-width half maximum (FWHM), θ is the Bragg angle, D is grain size and ε is the effective lattice strain.

Dislocation density:

The density of dislocations can be estimated by measurements made by Transmission Electron Microscopy (TEM) which gives more precision on a specific area of the thin layer or by calculations from X-ray diffraction data (XRD) [17]. The dislocation density of the crystal was evaluated using the formula.

$$\gamma = {}^{1}/_{D2} \quad (4)$$

Table 2: Parameters of XRD of sprayed CIGS films.

Sample	Grain Size (nm)	Dislocation density (nm^{-1})	Lattice strain (ε)
Sprayed CIGS1	429.82	$5.41.10^{-6}$	0.62
Sprayed CIGS2	546.26	$3.35.10^{-6}$	0.56
Sprayed CIGS3	567.22	$3.10.10^{-6}$	0.52

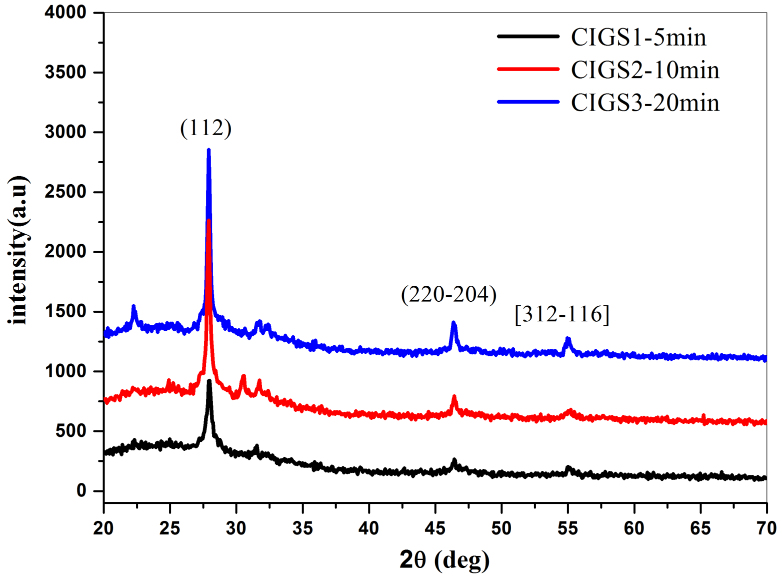

Fig 1. XRD results for sprayed CIGS with different annealing time.

Scanning electron microscopy (SEM):

The morphology of thin layers prepared by spray pyrolysis are examined by Scanning electron microscopy (SEM), the figures show that the surface is smooth of the three editions but there is a noticeable difference in the size of the grains and the density of the surface [18]. as we see that for the thin layer Sprayed CIGS1 that has been treated at 370 °C for 5min, we notice the appearance of the grains, but it is a little weak with a small size. for the thin layer sprayed CIGS2 or treated at a temperature of 370 °C hang 15 min there is the growth of the gains and compact surface, for the thin layer Sprayed CIGS3 treated at the same temperature 370 °C for 20 min the surface is compact, and the grains is dense with a large size. This shows that the treatment of the surface of the thin films at temperature 370 °C for 20 minutes plays a necessary role for the enlargement of the grain size which is considered important for the effectiveness of the absorber.

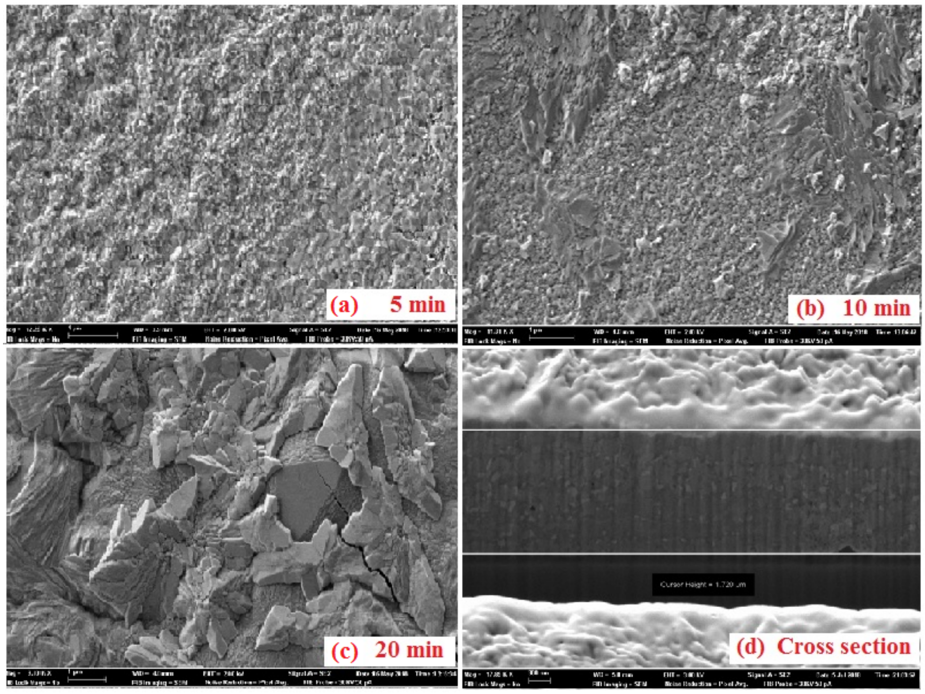

Fig 2. SEM images with different annealing time (a) CIGS1 for 5min, (b) CIGS2 for 10 min, (c) CIGS3 for 20 min and (d) Cross Section for CIGS 20 min.

Transmission electron microscopy (TEM):

Transmission electron microscopy is a direct method to have direct access to the size and shape of grains as well as the polydispersity of nanocrystals [19] the images took by Transmission electron microscopy shows that inter-plane distance of the grains is becoming larger with the duration of surface treatment of the thin layers prepared by spray pyrolysis.

The surface treatment time 5 min, 10 min and 20 min of the samples increases the inter planer distance of the samples 0.25 nm, 0.28 nm and 0.36 nm respectively.

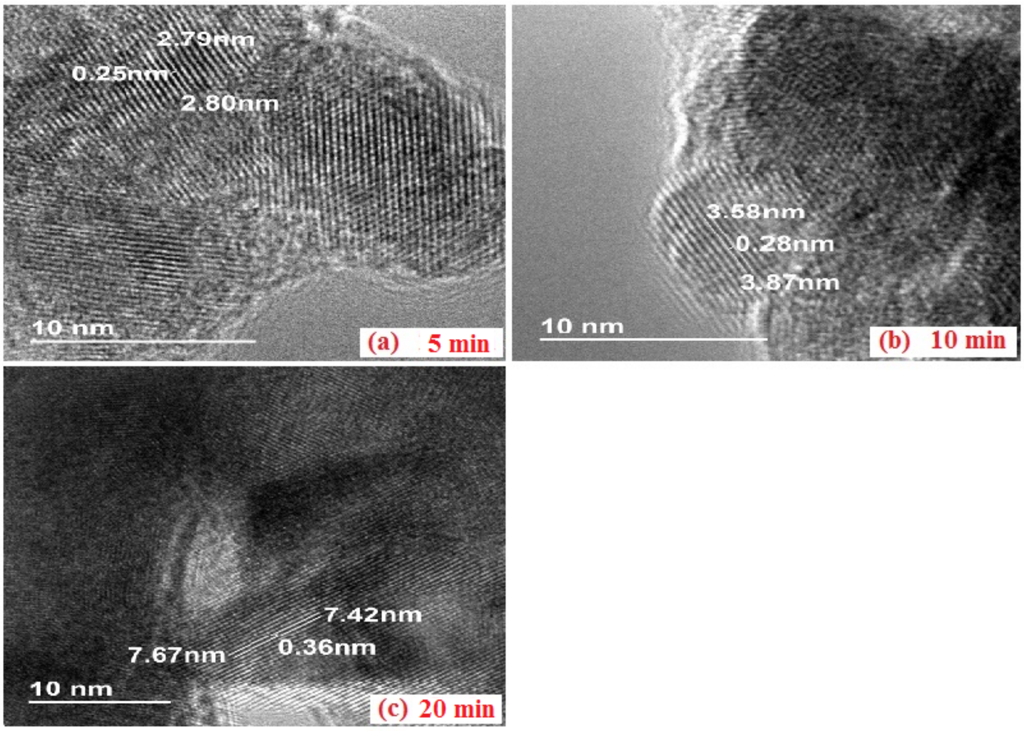

Fig 3. TEM images (a) CIGS1 for 5 min, (b) CIGS2 for 10 min and (c) CIGS3 for 20 min.

Atomic force microscopy (AFM):

Figure 4 shows 2D and 3D surface topography with difference in roughness and grain size of the films [20]. According to AFM analysis annealing time effect the roughness and the grain size of the samples which illustrate in table 3. The grain boundaries of the films become low due to increasing of the grain size to reduce the recombination rate and increase the device performance, which is favorable for the performance of solar cells as the roughness increases to trap more light.

A. Bouich et al. Applied Physics A (2019) 125:579
https://doi.org/10.1007/s00339-019-2874-4

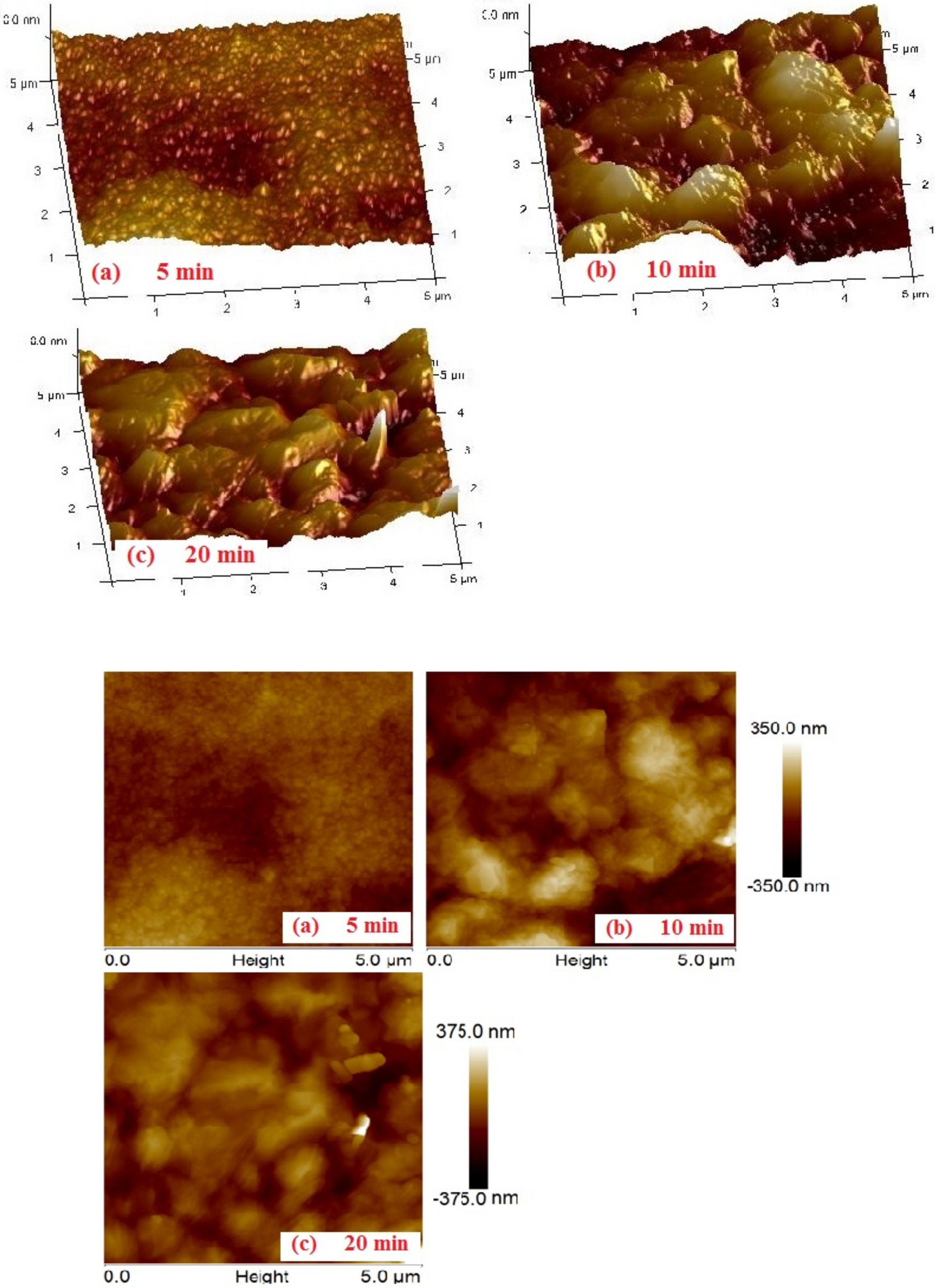

Fig 4. **2D and 3D** AFM images of CIGS thin_films (a) CIGS1 5 min, (b) CIGS2 10 min and (c) CIGS3 20 min.

Sample ID	Roughness (nm)	Grain Size (nm)
Saryed-CIGS1 5min	318	429.82
Sprayed-CIGS2 10min	490	546.26
Sprayed-CIGS3 20min	751	567.22

Table 3: Roughness and Grain Size of CIGS thin films prepared by Spray pyrolysis.

Optical proprieties:

Absorbance, transmittance and gap energy:

Annealing temperature and annealing time have an impact on the optical properties and the optical constants which are very important for the efficiency of a semiconductor [21]. The absorbance figure shows that the absorption is very remarkable for the sprayed CIGS3 sample or it is treated at a 370 °C temperature for 20 min and it has been recorded in the wavelength range (400 nm to 900 nm). It is found that all the films have a high absorbance and a low transmittance. There is a small difference in the results in terms of percentage (%) of the absorbance and transmittance of the films. The highest transmittance value is observed for the CIGS1 sprayed (25%) with annealing for 5 min and the CIGS3 film with a lower transparency of 10%.

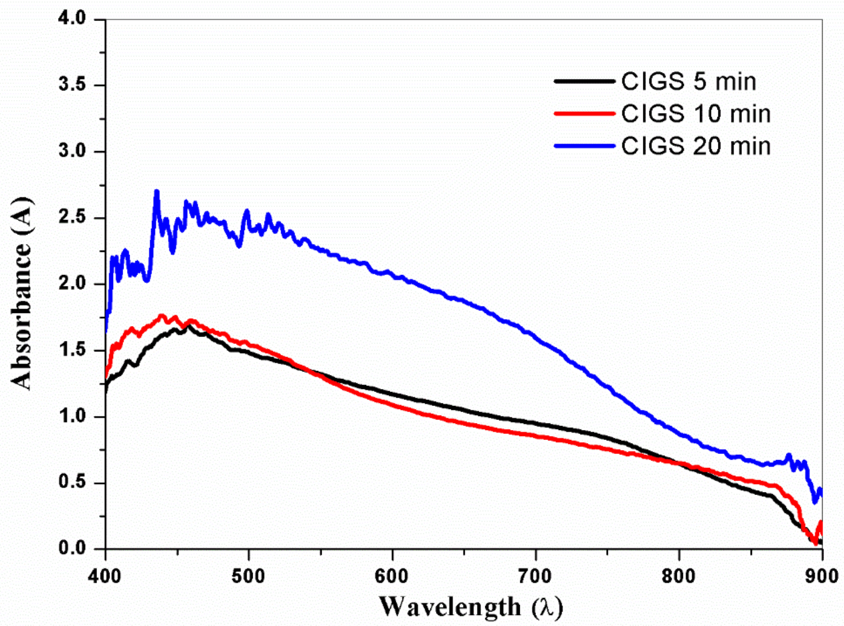

Fig 5. Optical absorbance of the CIGS thin films obtained by spray with annealing.

By processing the swings at a temperature 370 °C hang 20 min this shows high absorbance in the visible region with a maximum value of about 1.15.

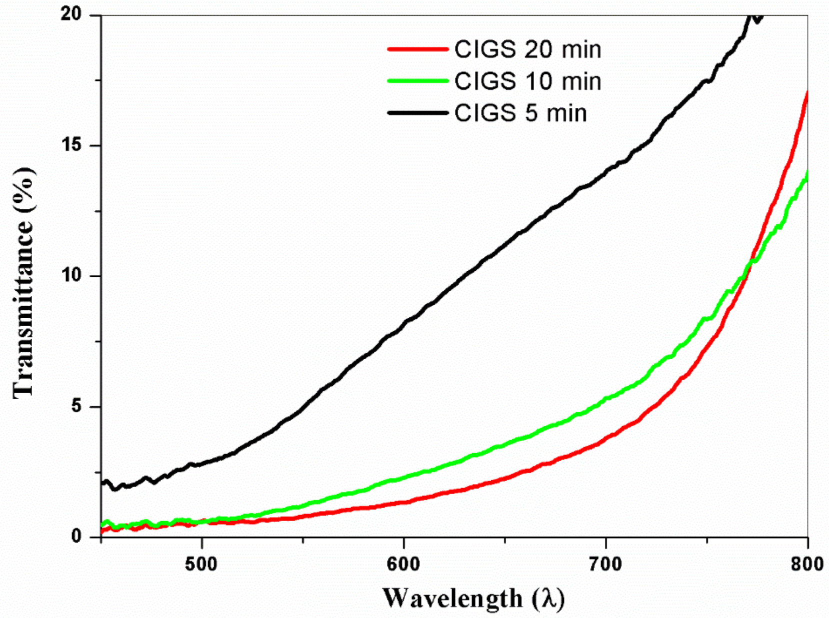

Fig 6. Optical transmittance of the CIGS thin films.

to calculate the gap energy of the thin films prepared we use the following equation and it conclude from the linear diagram of $(\alpha h\upsilon)^2$ versus $h\upsilon$ [22].

$$(\alpha h\upsilon)^2 = B\,(h\upsilon - E_g) \qquad (2)$$

where α is absorption coefficient and its calculated by equation (3), h is Planck constant, B is a constant, E_g is the band gap energy and t is the thickness of the thin films.

$$\alpha = \frac{1}{t}\ln\left(\frac{1}{T}\right) \qquad (3)$$

The calculated values of band gap energy are 1.66 eV for sample sprayed CIGS1, 1.62 eV for Sprayed CIGS2. For sample Sprayed CIGS3, a strong absorbance and band gap energy of the order of 1.46 eV make the films annealed at Temperature 370 ºC hang 20 min a good choice for solar cells application [10].

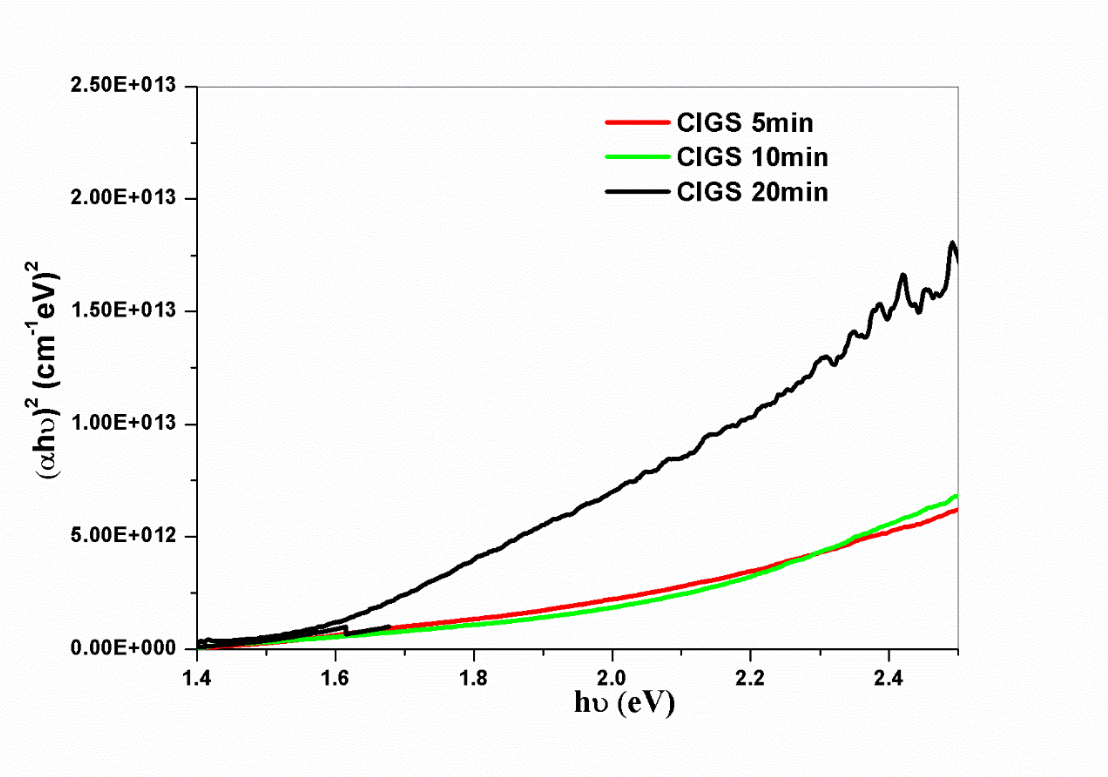

Fig 7. Optical absorbance of the CIGS thin films.

Optical constants

The optical constants, namely refractive index (n), extinction coefficient (k), real part (ε_r) and imaginary part (ε_i) of dielectric constant for CIGS, which were calculated using Eqs (4), (5), (6) and (7) whose values are presented in table 1 [23].

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \quad (4)$$

$$K = \frac{\alpha\lambda}{4\Pi} \quad (5)$$

$$\varepsilon_r = n^2 - k^2 \quad (6)$$

$$\varepsilon_i = 2nk \quad (7)$$

where n is the refractive index, k is the extinction coefficient, λ is the wavelength, α is the absorption coefficient and R is the reflectance of the films. The value of refractive index for the films spayed is attributed to the thickness of the films. The high extinction coefficient value is observed for this spayed CIGS3 due to the high absorption into this film compared by anthers.

The high extinction coefficient values are attributed to the absorbance.

The both real and imaginary part of dielectric constant decrease with the wavelength and the maximum values are observed on the sample sprayed CIGS3 (see Table 1).

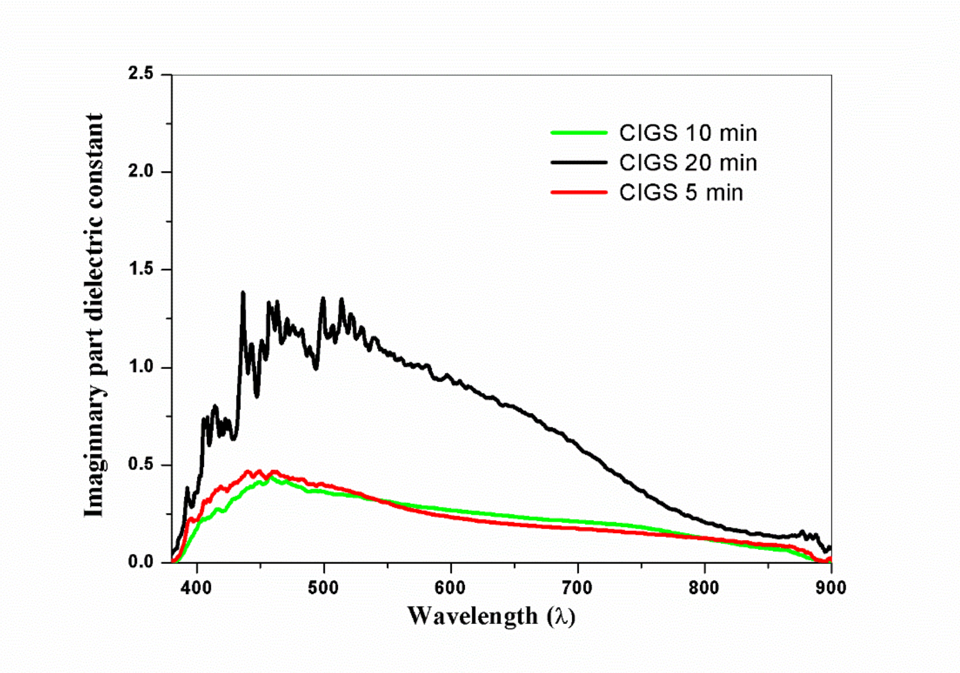

Fig 8. Imaginary part dielectric constant of the CIGS thin films.

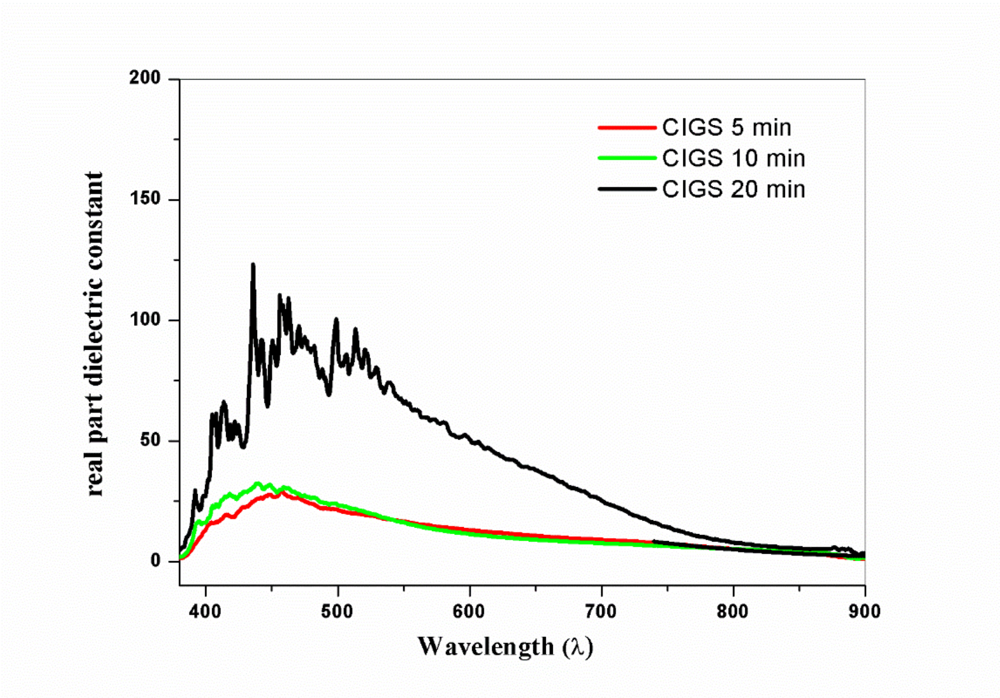

Fig 9. real part dielectric constant of the CIGS thin films.

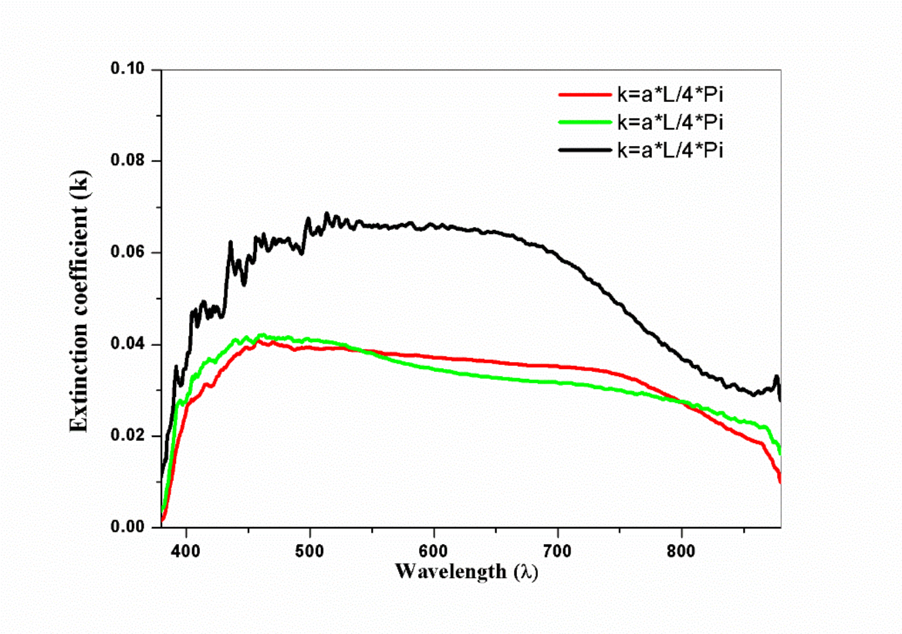

Fig 10. Extinction coefficient of the CIGS thin films.

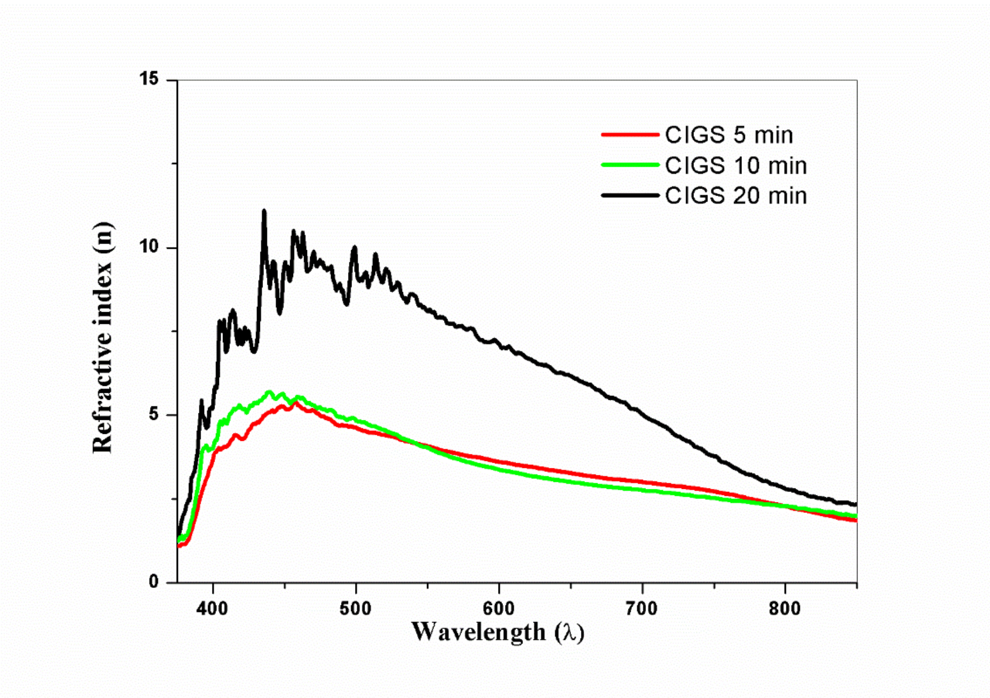

Fig 11. Refractive index of the CIGS thin films.

Table 4. Optical properties of the CIGS thin films.

Precursor	n	k	ε_r	ε_i
Sprayed CIGS1-5min	4	0.03	12.5	0.25
Sprayed CIGS2-10min	4	0.03	12.5	0.25
Sprayed CIGS3-20min	5	0.04	14	0.37

Electrical properties

Hall effect measurements gave us several information on electrical properties, we used four prob methods to give electrical resistance using the equation below [18].

$$R = R_s \times t \qquad (9)$$

Where t is the thickness and R_s is the resistivity of the thin film.

The resistivity of the three thin layers is of the order of 10-2 (Ω.cm), the lowest is observed resistivity values for the layers are annealed and the resistivity it is in order of of 0.65 (Ω. cm) for all samples. The values obtained by the reported work [18]. The low values of resistivity are attributed to the electrical nature of CIGS semiconductors. The concentration and mobility of the charge carriers in the CIGS layers are determined by Hall effect measurements [24]. The measurements made by the Hall effect allowed us to determine the resistivity (R_s) where we found that it is the order of 10^{-2} Ω.cm and the mobility (μ) is of the order 10^2 cm^2 / V s and for the concentration in carriers (n) is the order 10^6 1 /cm^3 The mobility (μ_n) and the concentration (n) of the charge carriers are listed in table.

Table 5: Electrical properties of the CIGS thin films calculated using Van der pauw method.

Sample	Concentration (1/cm$^{3)}$	Rs (Ω / sq)	R (10^{-2} Ω.cm)	Conductivity (1/ Ω.cm)	Mobility (Cm^2/V s)
CIGS1-5 min	1.5 E+15	404.4	606.6	2.5 E+15	6.87 E+2
CIGS2-10 min	1.1 E+16	434.07	651.015	3.8 E+15	7.98E+1
CIGS3-20 min	1.2 E+16	435.01	652.605	0.8 E+15	8.74E+1

5-Conclusion:

The CIGS thin films were prepared and deposited by spray technique and treated with a 370 ºC annealing temperature at different annealing times. Thin films have been studied using several characterization techniques such as X-ray diffraction to calculate the lattice parameters effective lattice strain and Dislocation density. Scanning electron microscopy (SEM) shows that the surface is with a noticeable difference in grain size. Transmission electron microscopy (TEM) results is confirm strong relation that films are polycrystalline.

Atomic force microscopy (AFM) shows a remarkable relation with the grain size and roughness of the surface of the films. The high absorbance and low transmittance are observed for the films prepared with a bang gap energy of approximately 1.46 eV. Optical constants such as refractive index (n), extinction coefficient (k), real part (εr) and imaginary part (εi) of the dielectric constant were extracted by Absorbance / transmittance data.

The carrier concentration, the mobility, the resistivity and the conductivity for the films treated at a 370 °C time for 20 minutes are 1.2 E+16 1/cm^3, 652.60 10^{-2} Ω.cm,0.8 E+15 1/ Ω.cm, 8.74E+1 cm^2/V s respectively. By considering the values found for the electrical properties, it is proposed that the annealing time of 20 min under a temperature of 370 ºC is the right choice for the development of solar cells based on $CuInGaS_2$.

Acknowledgments

Prof. Bouchaib HARTITI, Senior Associate at ICTP, is very grateful to ICTP for permanent support. Prof. Mohamed Ebn touhami, Director of the University Center for Analysis, Expertise, Transfer of Technology and Incubation, Kenitra, Morocco, is very grateful to CUA2TI for financial support. Thanks to Doctor Diogo M.F. Santos for the supervision of Amal Bouich's work during her research in CeFEMA research center. The authors also thank researchers from CeFEMA, (IST-ULisboa, Portugal) and CUA2TI (FS-Kenitra Morocco) for their help.

References:

[1] Sajeesh, T. H., Warrier, A. R., Kartha, C. S., & Vijayakumar, K. P. (2010). Optimization of parameters of chemical spray pyrolysis technique to get n and p-type layers of SnS. *Thin Solid Films*, *518*(15), 4370-4374.

[2] Wang, H. C., Wang, C. C., Feng, S. W., Chen, L. H., & Lin, Y. S. (2013). Synthesis of CIGS thin film by solvothermal route. *Optical Materials Express*, *3*(1), 54-66.

[3] Feurer, T., Reinhard, P., Avancini, E., Bissig, B., Löckinger, J., Fuchs, P., ... & Buecheler, S. (2017). Progress in thin film CIGS photovoltaics–Research and development, manufacturing, and applications. *Progress in Photovoltaics: Research and Applications*, *25*(7), 645-667.

[4] Zegadi, A., Slifkin, M. A., Djamin, M., Hill, A. E., & Tomlinson, R. D. (1992). A photoacoustic study of CuInxGa1− xSe2 alloys. *physica status solidi (a)*, *133*(2), 533-540.

[5] Liu, J., Zhuang, D., Luan, H., Cao, M., Xie, M., & Li, X. (2013). Preparation of Cu (In, Ga) Se2 thin film by sputtering from Cu (In, Ga) Se2 quaternary target. *Progress in Natural Science: Materials International*, *23*(2), 133-138.

[6] Hossain, M. I. (2012). Fabrication and characterization of CIGS solar cells with In 2 S 3 buffer layer deposited by PVD technique. *Chalcogenide Letters*, *9*(5), 185-191.

[7] Mughal, M. A., Engelken, R., & Sharma, R. (2015). Progress in indium (III) sulfide (In2S3) buffer layer deposition techniques for CIS, CIGS, and CdTe-based thin film solar cells. *Solar Energy*, *120*, 131-146.

[8] Powalla, M., Cemernjak, M., Eberhardt, J., Kessler, F., Kniese, R., Mohring, H. D., & Dimmler, B. (2006). Large-area CIGS modules: Pilot line production and new developments. *Solar Energy Materials and Solar Cells*, *90*(18-19), 3158-3164.

[9] Calixto, M. E., Sebastian, P. J., Bhattacharya, R. N., & Noufi, R. (1999). Compositional and optoelectronic properties of CIS and CIGS thin films formed by electrodeposition. *Solar energy materials and solar cells*, *59*(1-2), 75-84.

[10] Jung, S., Ahn, S., Yun, J. H., Gwak, J., Kim, D., & Yoon, K. (2010). Effects of Ga contents on properties of CIGS thin films and solar cells fabricated by co-evaporation technique. *Current Applied Physics*, *10*(4), 990-996.
[11] Ovshinsky, S. R., Deng, X., & Young, R. (1993). *U.S. Patent No. 5,231,047*. Washington, DC: U.S. Patent and Trademark Office.
[12] Kaelin, M., Rudmann, D., & Tiwari, A. N. (2004). Low cost processing of CIGS thin film solar cells. *Solar Energy*, *77*(6), 749-756.
[13] Shirakata, S., Kannaka, Y., Hasegawa, H., Kariya, T., & Isomura, S. (1999). Properties of Cu (In, Ga) Se2 thin films prepared by chemical spray pyrolysis. *Japanese journal of applied physics*, *38*(9R), 4997.
[14] Shirakata, S., Kannaka, Y., Hasegawa, H., Kariya, T., & Isomura, S. (1999). Properties of Cu (In, Ga) Se2 thin films prepared by chemical spray pyrolysis. *Japanese journal of applied physics*, *38*(9R), 4997.
[15] Kumar, Y. K., Babu, G. S., Bhaskar, P. U., & Raja, V. S. (2009). Effect of starting-solution pH on the growth of Cu2ZnSnS4 thin films deposited by spray pyrolysis. *physica status solidi (a)*, *206*(7), 1525-1530.
[16] Ajili, M., Castagné, M., & Turki, N. K. (2014). Characteristics of CuIn1− xGaxS2 thin films synthesized by chemical spray pyrolysis. *Journal of Luminescence*, *150*, 1-7.
[17] Babu, B. J., Velumani, S., Kassiba, A., Asomoza, R., Chavez-Carvayar, J. A., & Yi, J. (2015). Deposition and characterization of graded Cu (In1-xGax) Se2 thin films by spray pyrolysis. *Materials Chemistry and Physics*, *162*, 59-68.
[18] Shirakata, S., Kannaka, Y., Hasegawa, H., Kariya, T., & Isomura, S. (1999). Properties of Cu (In, Ga) Se2 thin films prepared by chemical spray pyrolysis. *Japanese journal of applied physics*, *38*(9R), 4997.
[19] Frantz, J. A., Bekele, R. Y., Nguyen, V. Q., Sanghera, J. S., Bruce, A., Frolov, S. V., ... & Aggarwal, I. D. (2011). Cu (In, Ga) Se2 thin films and devices sputtered from a single target without additional selenization. *Thin Solid Films*, *519*(22), 7763-7765.
[20] Calderón, C., Gordillo, G., Bartolo-Pérez, P., & Mesa, F. (2007). Effect of the deposition conditions on the optical, morphological and compositional properties of CuIn1− xGaxSe2 thin films prepared by a multistage process. *Revista Mexicana de Física*, *53*(7), 270-273.
[21] Schmid, D., Ruckh, M., Grunwald, F., & Schock, H. W. (1993). Chalcopyrite/defect chalcopyrite heterojunctions on the basis of CuInSe2. *Journal of Applied Physics*, *73*(6), 2902-2909.
[22] Matur, U. C., Akyol, S., Baydoğan, N., & Cimenoglu, H. (2015). The Optical Properties of CIGS Thin Films Derived by Sol-gel Dip Coating Process at Different Withdrawal Speed. *Procedia-Social and Behavioral Sciences*, *195*, 1762-1767.
[23] Pankove, J. I. (1975). *Optical processes in semiconductors*. Courier Corporation.
[24] Matsumura, K., Fujita, T., Itoh, H., & Fujita, D. (2014). Characterization of carrier concentration in CIGS solar cells by scanning capacitance microscopy. *Measurement Science and Technology*, *25*(4), 044020.