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Application of Taguchi approach to optimize the sol–gel process of the quaternary Cu_2ZnSnS_4 with good optical properties

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ABSTRACT

Present research deals with the optimal deposition parameters configuration for the synthesis of Cu_2ZnSnS_4 (CZTS) thin films using the sol–gel method associated to spin coating on ordinary glass substrates without sulfurization. The Taguchi design with a L9 (3^4) orthogonal array, a signal-to-noise (S/N) ratio and an analysis of variance (ANOVA) are used to optimize the performance characteristic (optical band gap) of CZTS thin films. Four deposition parameters called factors namely the annealing temperature, the annealing time, the ratios Cu/(Zn + Sn) and Zn/Sn were chosen. To conduct the tests using the Taguchi method, three levels were chosen for each factor. The effects of the deposition parameters on structural and optical properties are studied. The determination of the most significant factors of the deposition process on optical properties of as-prepared films is also done. The results showed that the significant parameters are Zn/Sn ratio and the annealing temperature by applying the Taguchi method.
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1. Introduction

Kesterite Cu_2ZnSnS_4 (CZTS) is a quaternary semiconducting compound which has emerged over the past decade as an absorber layer in thin films photovoltaics. This material is considered to be the principal replacement of the chalcopyrite CIGS which has already proved to be successful for photovoltaic applications and is already with CdTe thin film solar cell at the commercialization stage [1]. But because of expensive, scarce and toxic elements like indium, gallium and tellurium which affect the large scale productions, all interests are turned to the CZTS owing to the high natural abundance and non-toxicity of all its constituents [2–4]. Thanks to its similar properties to the CIGS material, the CZTS compound is a good candidate as an absorber layer for thin film solar cells applications [5–8]. It has a tunable and direct band gap energy ranging from 1.4 to 1.6 eV, a high absorption coefficient over 10^4 cm^{-1} and p-type conductivity [9]. However, although it showed very good properties adequate with photovoltaic applications, the studies on CZTS-based solar cells are still at an early stage beginning from the material synthesis until the fabrication of the entire cell [10]. A record efficiency of 12.6% has been reported for CZTS-based solar cell in laboratory conditions [11]. Many studies are carried out to improve the efficiency and to develop simple and economical fabrication methods. CZTS thin films have been synthesized using various methods including physical vapor deposition [6,8,10,12–20], electrodeposition [21–24], sol–gel method [25–34], spray pyrolysis [35,36] … Solution-based deposition methods have a lot of advantages for instance a variety of thin films can be synthesized at low temperatures using cheap manufacturing equipments. Among the solution-based deposition methods, the sol–gel is one of the most simple and low cost process based on hydrolysis and polycondensation reactions. Several groups have reported the synthesis of CZTS thin films by sol–gel method [29–31]. But it is still necessary to increase the quality of sol–gel processed CZTS thin films by improving the synthesis process as well as by determining the best combination of deposition parameters which lead to best optical properties of CZTS. The physical properties of CTZS films depend highly on the deposition technique and the deposition parameters [37]. The change in material properties that occurs with deposition parameters composition could be

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due to the presence of defects. Binary and ternary phases in CZTS film affect their optical and electronic properties.

In this study, we want to obtain the optimal properties (band gap energy) of CZTS thin films prepared by sol gel method without sulfurization. For that, we used the Taguchi method in order to find the best deposition parameters combination. The effect of deposition parameters on structural, morphological and optical properties is also studied using x-ray diffraction (XRD), atomic force microscopy (AFM) and UV–Vis–NIR spectrophotometry.

2. Experimental

2.1. Film preparation and characterization

The Cu_2ZnSnS_4 (CZTS) thin films were prepared by the sol–gel method and deposited on ordinary glass substrates by the spin coating technique. The deposition solution is made of copper II chloride, zinc II chloride, tin IV chloride and thiourea dissolved in 2-methoxyethanol and monoethanolamine used respectively as the solvent and the stabilizer. A clear yellow solution was formed after adding thiourea and was stirred for half an hour at 50 °C. Before deposition, the glass substrates were cut in dimensions $25 \times 25 \times 1$ mm^2 and cleaned into acetone, distilled water and ethanol for a few minutes. To prepare thin films, the prepared solution was filtered and spin-coated on substrates at 2500 rpm for 30s followed by a solvent drying at 200 °C for 5 min on a hot plate. The coated glasses were annealed in a nitrogen atmosphere at a fixed temperature and a fixed time. The crystal structures of the films were determined by X-ray diffraction and Raman spectroscopy, the surface topography was performed by an atomic force microscope (AFM). The optical absorbance spectra of films for the calculation of the optical band gap energies were recorded using an UV–Vis–NIR spectrophotometer in the wavelengths ranging from 200 to 1200 nm.

2.2. Taguchi method

The first thing to do in designing any experiment is the recognition of the problem. This means to select the effective factors able to have a significant effect on a specifying response variable that we want to optimize. Then, based on the objectives, one must choose a suitable experimental design and execute experiments accordingly. The measured data from the experiments can be analyzed using statistical tools like signal-to-noise ratio (S/N) and analysis of variance (ANOVA) method to determine the factors with a significant influence on the response variable. It is important to note that the choice of the experimental design depends on the type of the problem, the number of factors and their levels.

The Taguchi approach, more effective than traditional design of experiment such as factorial design, has achieved a great deals of success. It considers two types of factors namely the control factor and the noise factor to study the influence of different parameters on the mean and variance of a process performance characteristic that defines the effectiveness of the process [38–40]. The overall aim of the Taguchi method is to find factor levels that maximize the signal-to-noise ratio. In this study, the Taguchi approach with a L9 (3^4) orthogonal array is used to find the optimal experimental conditions that lead to an optimal band gap energy for CZTS thin films prepared by sol–gel method. The process parameters are varied in order to determine the best deposition parameters for optimal band gap energy of CZTS thin films. Table 1 shows the factors and their levels for the CZTS synthesis. Each experiment was repeated twice for the reproducibility of result and the average of two values was subsequently used for the calculation of the S/N ratio. The optimal values were therefore determined by comparing the resulting S/N ratio. In this study, the optimization of the process parameters that lead to good optical properties of CZTS thin films is based on the following formula:

Table 1
Factors and their levels for the CZTS preparation conditions.

Symbol	Factor	Level		
		Level 1	Level 2	Level 3
A	Annealing temperature (°C)	240	280	320
B	Annealing time (min)	30	45	60
C	[Cu]/([Zn]+[Sn])	0.92	0.95	0.98
D	[Zn]/[Sn]	1	1.05	1.1

$$\Delta E_g = |E_{th} - E_{exp}| \quad (1)$$

Where ΔE_g is the difference between the theoretical optimal value of 1.5 eV [41,42] and the experimental value of CZTS energy band gap obtained from our experiments. The value ΔE_g=0 represents films with very good optical properties while higher values can show the presence of secondary or ternary phases like ZnS, SnS, Cu_2S or Cu_2SnS_3 which have a detrimental effect on CZTS performance. The goal with the Taguchi method is then to reduce the gap between these two values. The S/N ratio for the smaller the better performance characteristic is expressed as follows [43,44]:

$$S/N_i = -10 \log \left[1/n \sum_{j=1}^{n} Y_{ij}^2 \right] \quad (2)$$

Where i is an experiment, n the number of the measured values in the experiment i, Y_{ij}, the measured values of the experiment i and j=1,…,n.

In this study, MINITAB version 17.1.0 which is software for the automatic design and analysis of Taguchi experiments was used to analyze the results and to optimize the experiment conditions for setting the control variables. We haven't judged necessary to take into account interactions between factors because according to Taguchi, the interactions between many factors are always negligible except if the interactions between two factors are well identified. In addition there is more to gain by multiplying the number of tested factors than dwell on interactions problems.

3. Results and discussion

The S/N ratio and analysis of Variance (ANOVA) were used to determine the optimal levels of factors, to understand the significance of the process parameters effects on the experimental responses and to estimate also the errors due to the different combination of parameters. Table 2 shows the measured data for the optical band gap energy and the associated S/N ratios. Fig. 1

Table 2
Measured values of the band gap energy and the corresponding S/N ratios.

Experiment	Control factors				Gap energy		ΔE		S/N ratio
	A	B	C	D	E1	E2	$\Delta E1$	$\Delta E2$	
1	1	1	1	1	1.96	1.95	0.46	0.45	6.839
2	1	2	2	2	1.87	1.84	0.37	0.34	8.987
3	1	3	3	3	1.54	1.53	0.04	0.03	29.031
4	2	1	2	3	1.50	1.54	0	0.04	30.969
5	2	2	3	1	1.58	1.56	0.08	0.06	23.010
6	2	3	1	2	1.59	1.55	0.09	0.05	22.757
7	3	1	3	2	1.80	1.60	0.3	0.1	13.010
8	3	2	1	3	1.52	1.52	0.02	0.02	33.979
9	3	3	2	1	2.07	2.08	0.57	0.58	4.806

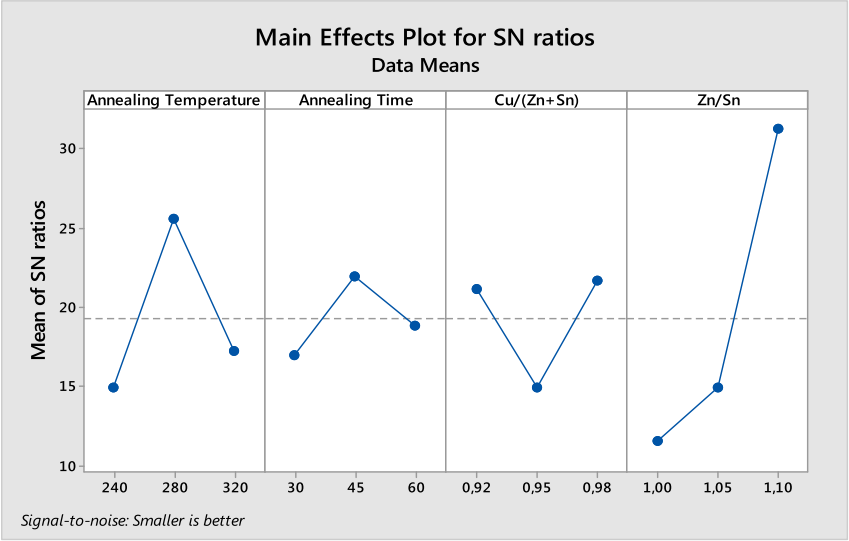


Fig. 1. The means of the S/N ratios graphs.

Table 3
ANOVA results.

Factor	Degree of freedom	Sum of square	Variance	Contribution P (%)	F-Variance ratio
A	2	187.37	93.69	19	5
B	2	39.02	19.51	4	
C	2	85.31	42.66	9	2
D	2	671.56	335.78	68	17
Error	0	0			
Total	8	983.26		100	
Estimated error	2	39.02	19.51		

shows the graphs of the S/N ratios means of the deposition parameters. From Fig. 1, it is seen that the parameters of the synthesis process have different effects on the band gap energy of CZTS thin films. The more influent parameter of the process is the Zn/Sn ratio as it shows the greater value of the S/N ratio followed respectively by the annealing temperature, the Cu/(Zn + Sn) ratio and the annealing time. This classification is expected because it was reported that a Cu-poor and Zn-rich CZTS exhibits very good properties. An optimal value of the Zn/Sn ratio allows having a Zn-rich CZTS and also allows avoiding secondary phases like Cu_xS, principal source of the band gap broadening in CZTS material. It can be said that the high band gap observed in certain films may be attributed to the residual organic precursor compounds of the sample at relatively low annealing temperatures [45]. So a suitable annealing temperature can also allow avoiding many impurities such as ZnS, Cu_xS or Cu_2SnS_3 which are also detrimental on optical properties of CZTS thin films.

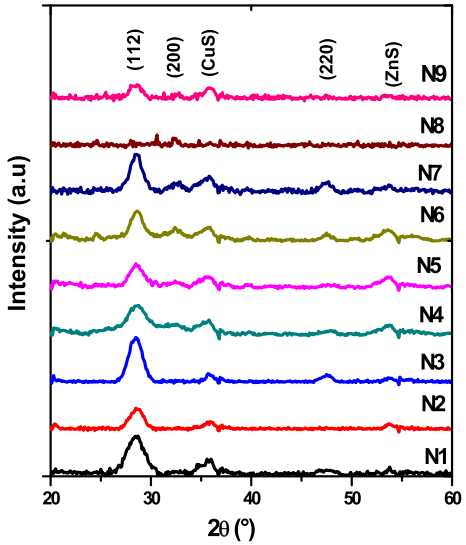


Fig. 2. XRD patterns of CZTS thin films for the Taguchi L9 orthogonal array from sample N1 to N9.

It is therefore important to control and to adjust the amount of the Zn/Sn ratio as well as the annealing temperature in the synthesis of CZTS thin films using the sol–gel method in order to have good optical properties. As shown in Fig. 1, the factors combination $A_2B_2C_3D_3$ (i.e. annealing temperature = 280 °C, annealing time = 45 min, Cu/(Zn + Sn) ratio = 0.98 and Zn/Sn ratio = 1.1) can be considered as the best combination of process parameters that leads to optimal band gap energy for CZTS thin films but needs a confirmation test to be validated. This combination could be the more efficient (robust) compared with the deviations included by noise factors if it is validated by the confirmation test. Moreover, the graphical analysis of the factors effects does not give information about the contribution of each factor on the response variable. This can be done by the ANOVA. Table 3 lists the corresponding ANOVA results where the contribution of each parameter on the response is presented. Since the interactions between factors cannot be taken into account, cross and quadratic terms don't appear in the ANOVA analysis. It is seen that the effect of the annealing time (factor B) and the Cu/(Zn + Sn) ratio (factor C) is relatively insignificant. However, the Zn/Sn ratio (factor D) has a

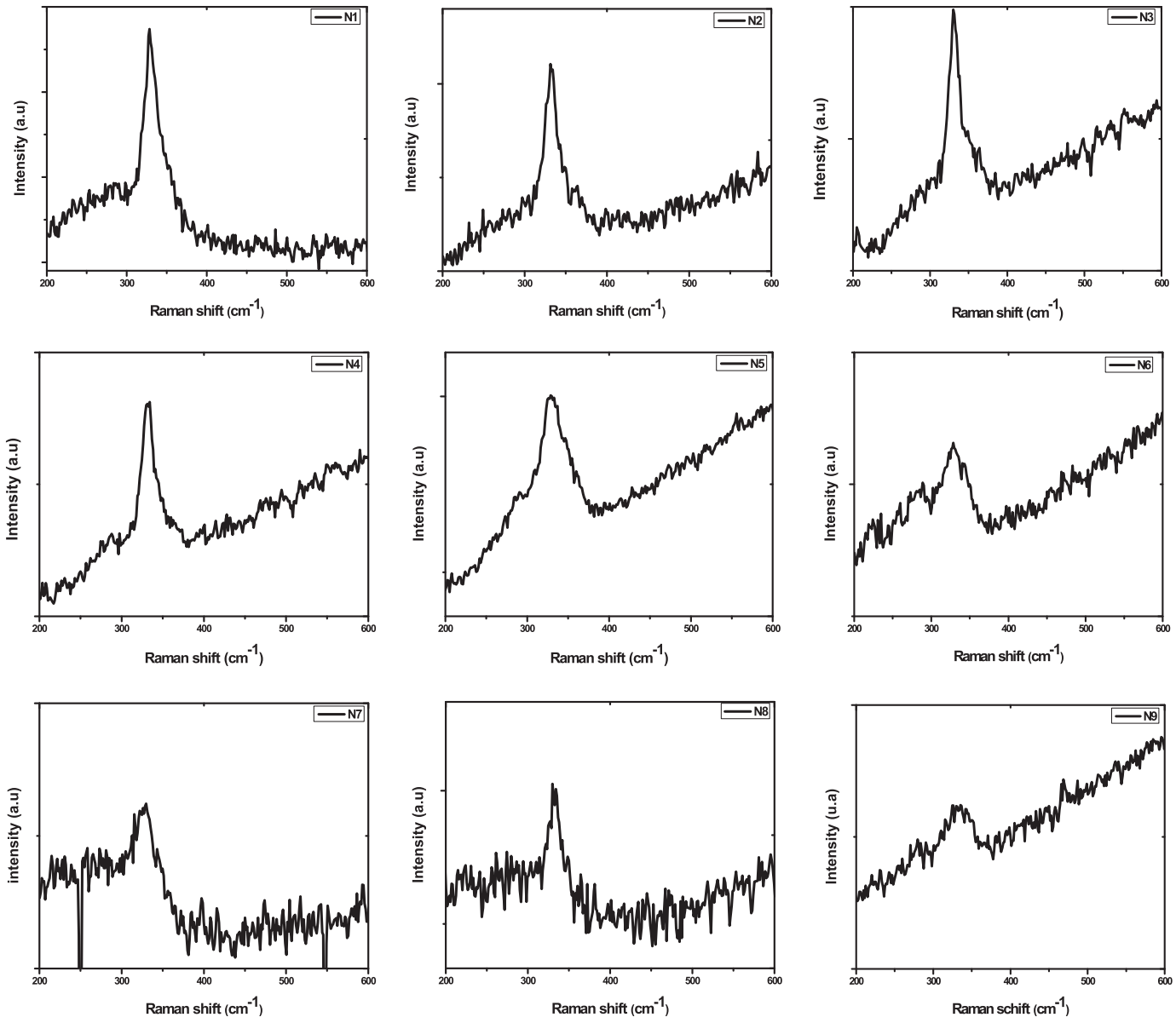


Fig. 3. Raman spectra of CZTS thin films for the Taguchi L9 orthogonal array from N1 to N9.

significant effect on the CZTS band gap energy with 68% of contribution, followed by the annealing temperature (factor A) with 19% of contribution. In addition, the Zn/Sn ratio with a F-ratio = 17 has a dominant effect followed by the annealing temperature with a F-ratio = 5 which has also a dominant effect but less than the Zn/Sn ratio.

The Cu/(Zn + Sn) ratio has a middle effect and the annealing time has been used to constitute the variance of the estimated error since the degree of the freedom of the error is equal to zero. These results are in good agreement with the result of the S/N ratio which showed that the Zn/Sn ratio and the annealing temperature are parameters physically and statistically significant in the synthesis of CZTS thin films using the sol–gel method. Fig. 2 shows the X-ray diffraction (XRD) patterns for the CZTS thin films prepared by sol–gel spin coating technique of the 9 experiments of the Taguchi L9 orthogonal array. All the films showed a polycrystalline structure with peaks identified at 28.5°, 32.37° and 47.61° positions assigned respectively to the crystallographic directions (112), (200) and (220) with a preferential direction along (112) axis and corresponding to the kesterite phase of the CZTS material [36,46,47]. Nevertheless, it is sometimes difficult to identify Cu_2ZnSnS_4 (CZTS), Cu_2SnS_3 (CTS) and ZnS materials only by the XRD technique because of the close similarities between their peaks diffraction. The Raman spectroscopy is often used to have more insights into the phase identification. The Raman spectra of as-prepared CZTS thin films of 9 samples are shown in Fig. 3. Only one peak at the position 333 cm^{-1} has been identified in all films. This peak is close to the peak of CZTS thin film or mono grain powder reported in previous literature at around 338 cm^{-1} position [13]. The peak at 333 cm^{-1} can be attributed to the Raman characteristic peak of CZTS. No additional peak was found in films confirming the pure nature of CZTS in films.

Fig. 4 shows the AFM 3D-micrographs of the 9 samples of CZTS thin films. The surface of all films is seen to be rough and the vertical height between the highest features (brightest) and lowest (darkest) is in the range of 0.07and 0.507 μm indicating that the

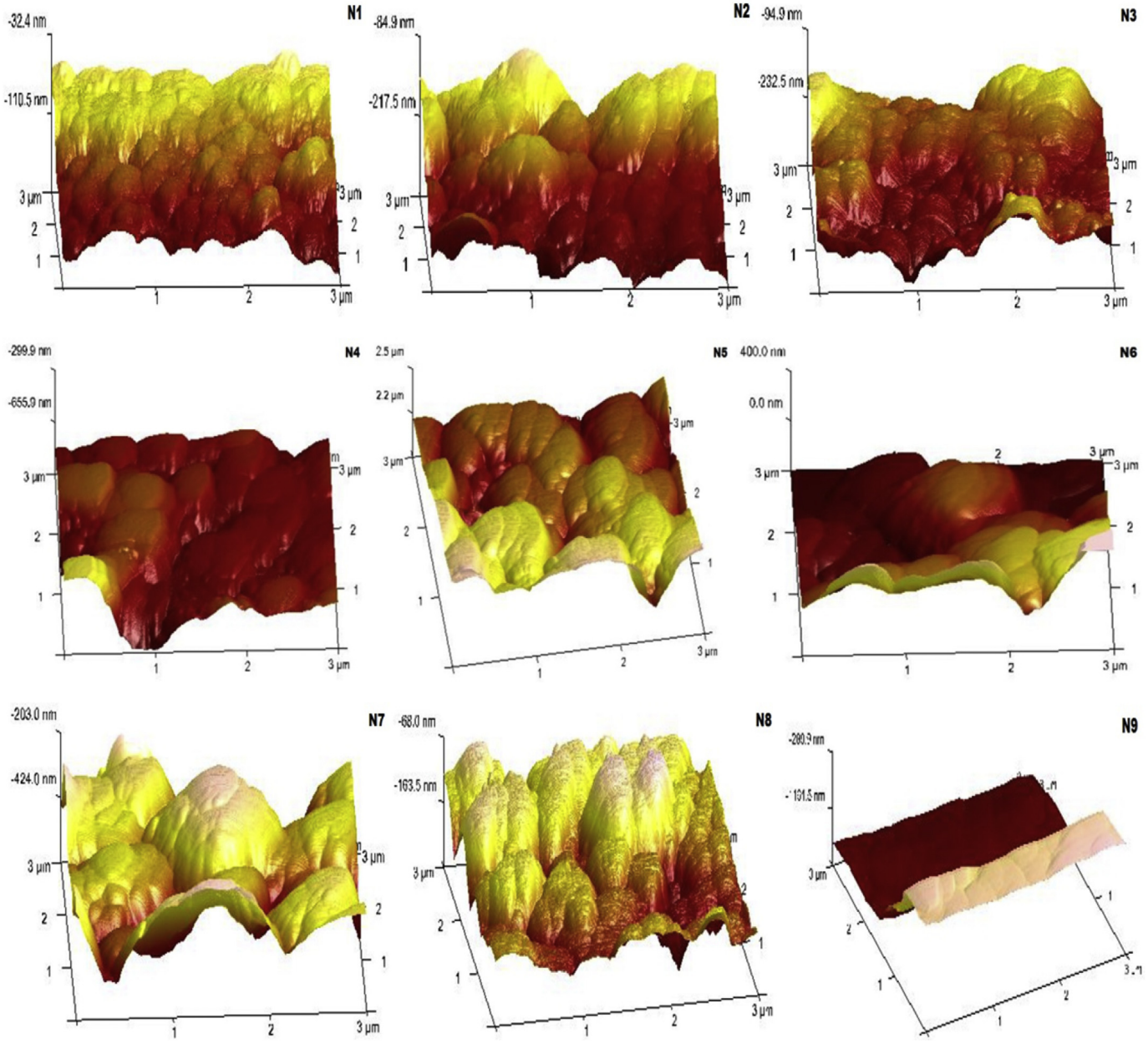


Fig. 4. 3D-micrographs of CZTS thin films for Taguchi L9 orthogonal array from N1 to N9.

surface is not quite homogeneous. Based on the AFM micrographs, the average roughness and the root-mean-square roughness (RMS) of the nine CZTS thin film samples prepared by sol–gel method using a L9 orthogonal array are lists in Table 4. The high values of the root-mean-square roughness observed in N4, N6, N7 and N9 films can be explained by the presence at the surface of these films agglomerations with big sizes. At certain temperatures particularly at higher temperatures, micro-crystallites observed at lower temperatures agglomerate and the consequence of this agglomeration is the formation of clusters onto the surface of the films with various dimensions [36].

In order to evaluate the band gap energy, the absorbance spectra of the CZTS films were measured in the wavelength range of 200–1200 nm using a UV–Vis–NIR spectrophotometer. In the case of direct allowed transitions, the absorption coefficient follows the spectral dependence giving by the following formula [48]:

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \tag{3}$$

Where A is a constant, $h\nu$ the energy of photons and E_g the corresponding semiconductor band gap energy. The optical band gap of the as-prepared CZTS films were estimated by extrapolating the linear part of the spectrum $(\alpha h\nu)^2 = f(h\nu)$ to zero of the absorption as seen in Fig. 5. The values of optical band gap of films are ranging from 1.52 to 2.08 eV and are comparable with CZTS band

Table 4
Average and root-mean-square roughnesses.

Films	N1	N2	N3	N4	N5	N6	N7	N8	N9
rms (nm)	11	24.3	29.7	66.8	60.4	112	88.2	24.9	194
Ra (nm)	8.69	19.5	23.3	50.1	47.4	85.0	69.8	19.4	161

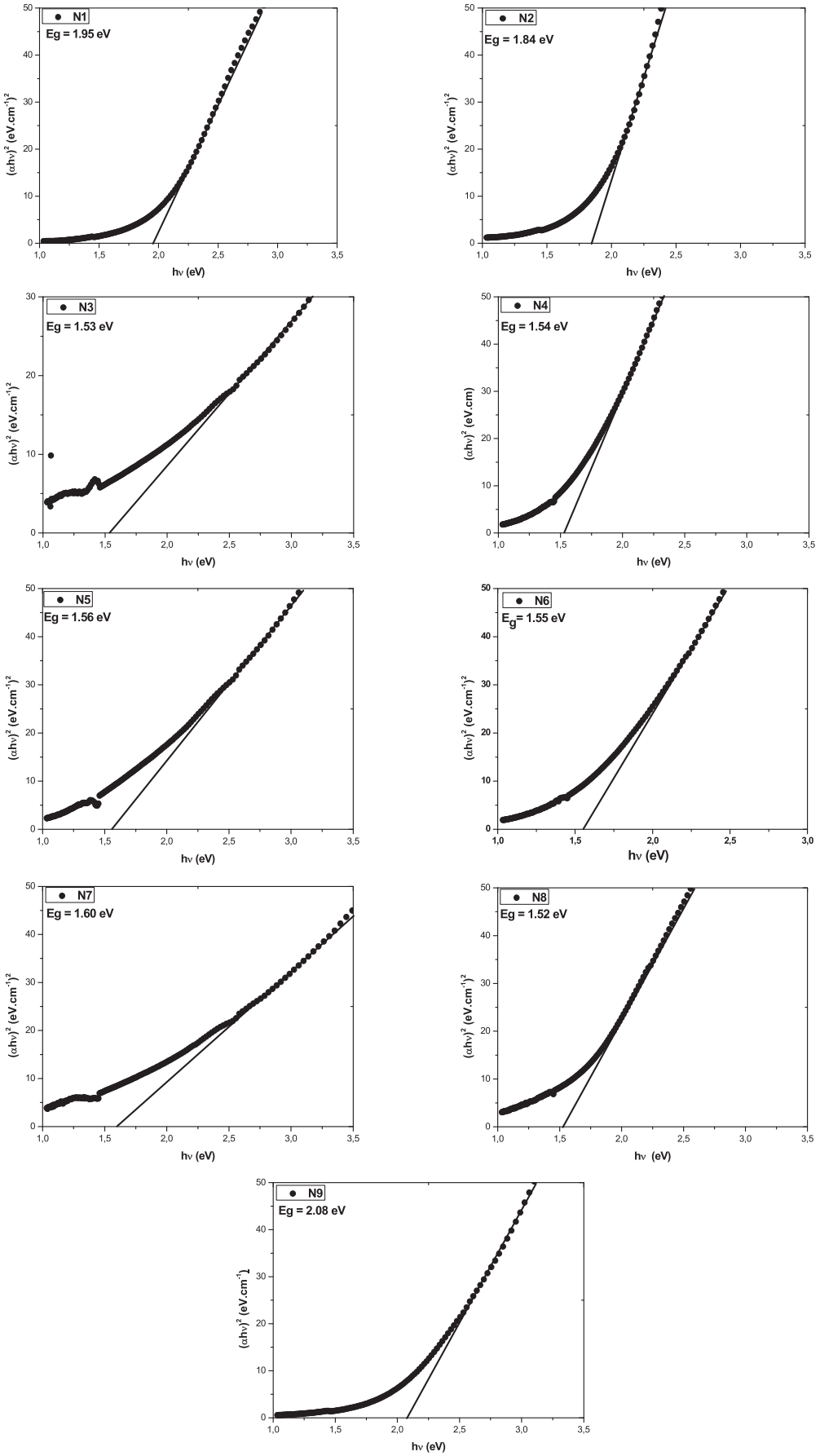


Fig. 5. $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) of all CZTS thin films for the Taguchi L9 orthogonal array from N1 to N9.

gap found by many authors [33,36 and 51]. The majority of these values lie in the optimal band gap range of 1.4–1.6 eV for CZTS semiconductor [45,49,50]. These optical properties show that the as-prepared films are suitable for applications in thin film solar cells.

4. Conclusions

In this study, the Taguchi L9 (3^4) orthogonal array is used to optimize the optical band gap of CZTS thin films prepared by sol–gel method without sulfurization with various process parameters. From characterization results, the XRD showed that all films have a polycrystalline structure with a preferential orientation along the (112) direction corresponding to a kesterite phase. The Raman spectroscopy confirmed the presence of CZTS and no other additional phase was found indicating a pure CZTS in films. The films showed for the majority an optical band gap in the range of 1.4–1.6 eV suitable for photovoltaic applications. From statistical analysis, the S/N ratio and ANOVA results have allowed to find that the near optimal combination of factors levels leading to optimal band gap of 1.5 eV for CZTS thin film is $A_2B_2C_3D_3$. But this combination needs to be validated by a confirmation test in order to be adopted. The dominant parameters of the CZTS thin film synthesis using sol–gel method are the Zn/Sn ratio and the annealing temperature. This study allowed understanding that the Taguchi approach can be used for practical synthesis processes in order to reduce effectively production costs, time and to achieve great improvements in CZTS film properties and quality.

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References

[1] H. Wang, Progress in thin film solar cells based on Cu_2ZnSnS_4, Int. J. Photoenergy 2011 (2011) 1–10, http://dx.doi.org/10.1155/2011/801292.
[2] C.B. Murray, D.J. Norris, M.G. Bawendi, Synthesis and characterization of nearly monodisperse CdE (E = sulfur, selenium, tellurium) semiconductor nanocrystallites, J. Am. Chem. Soc. 115 (1993) 8706–8715.
[3] A.K. Iwahori, R. Takagi, N. Kishimoto, I. Yamashita, A size controlled synthesis of CuS nano-particles in the protein cage, apoferritin, Mater. Lett. 65 (2011) 3245–3247.
[4] J. Tang, S. Hinds, S.O. Kelley, E.H. Sargent, Synthesis of Colloidal CuGaSe2, CuInSe2, and Cu(InGa)Se2 Nanoparticles, Chem. Mater 20 (2008) 6906–6910.
[5] K. Ito, T. Nakazawa, Electrical and optical properties of stannite-type quaternary semiconductor thin films, Jpn. J. Appl. Phys. 27 (1988) 2094–2097.
[6] H. Katagiri, K. Jimbo, S. Yamada, T. Kamimura, W.S. Maw, T. Fukano, T. Ito, T. Motohiro, "H_2S concentration dependence of properties of Cu_2ZnSnS_4 thin film prepared under non vacuum condition, Appl. Phys. Express 1 (2008) 041201.
[7] A. Ennaoui, M. Lux-Steiner, A. Weber, D. Abou-Ras, I. Kotschau, H.-W. Schock, R. Schurr, A. Holzing, S. Jost, R. Hock, T. Vob, J. Schulze, A. Kirbs, Cu_2ZnSnS_4 thin film solar cells from electroplated precursors: novel low-cost perspective, Thin Solid Films 517 (2009) 2511–2514.
[8] H. Katagiri, K. Saitoh, T. Washio, H. Shinohara, T. Kurumadani, S. Miyajima, Development of thin film solar cell based on Cu_2ZnSnS_4 thin films, Sol. Energy Mater. Sol. Cells 65 (2001) 141–148.
[9] W. Daranfed, M.S. Aida, N. Attaf, J. Bougdira, H. Rinnert, Cu_2ZnSnS_4 thin films deposition by ultrasonic spray pyrolysis, J. Alloys Compd. 542 (2012) 22–27.
[10] P.K. Sarswat, M. Snure, M.L. Free, A. Tiwari, CZTS thin films on transparent conducting electrodes by electrochemical technique, Thin Solid Films 520 (2012) 1694–1697.
[11] W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, D.B. Mitzi, Device characteristics of CZTSSe thin-film solar cells with 12.6% efficiency, Adv. Energy Mater 4 (2014) 1–5, 1301465.
[12] K. Wang, O. Gunawan, T. Todorov, B. Shin, S.J. Chey, N.A. Bojarczuk, D. Mitzi, S. Guha, Thermally evaporated Cu_2ZnSnS_4 solar cells, Appl. Phys. Lett. 97 (2010) 143508–143510.
[13] P.A. Fernandes, P.M.P. Salomé, A.F. daCunha, Growth and Raman scattering characterization of Cu_2ZnSnS_4 thin films, Thin Solid Films 517 (2009) 2519–2523.
[14] P.A. Fernandes, P.M.P. Salomé, A.F. daCunha, B.A. Schubert, Cu_2ZnSnS_4 solar cells prepared with sulphurized dc-sputtered stacked metallic precursors, Thin Solid Films 519 (2011) 7382–7385.
[15] P.A. Fernandes, P.M.P. Salomé, A.F. daCunha, Study of polycrystalline Cu_2ZnSnS_4 films by Raman scattering, J. Alloys Compd. 509 (2011) 7600–7606.
[16] H. Katagiri, Cu_2ZnSnS_4 thin film solar cells, Thin Solid Films 480–481 (2005) 426–432.
[17] B.A. Schubert, B. Marsen, S. Cinque, T. Unold, R. Klenk, S. Schorr, H.W. Schock, Cu_2ZnSnS_4 thin film solar cells by fast coevaporation, Prog. Photovoltaics Res. Appl. 19 (2011) 93–96.
[18] H. Araki, A. Mikaduki, Y. Kubo, T. Sato, K. Jimbo, W.S. Maw, H. Katagiri, M. Yamazaki, K. Oishi, A. Takeuchi, Preparation of Cu_2ZnSnS_4 thin films by sulfurization of stacked metallic layers, Thin Solid Films 517 (2008) 1457–1460.
[19] J.S. Seol, S.Y. Lee, J.C. Lee, H.D. Nam, K.H. Kim, Electrical and optical properties of Cu_2ZnSnS_4 thin films prepared by RF-magnetron sputtering process, Sol. Energy Mater. Sol. Cells 75 (2003) 155–162.
[20] T. Yamaguchi, T. Kubo, K. Maeda, S. Niiyama, T. Imanishi, A. Wakahara, Fabrication of Cu_2ZnSnS_4 thin films by sulfurization process from quaternary compound for photovoltaic device applications, in: The International Conference on Electrical Engineering, 2009.
[21] S.M. Pawar, B.S. Pawar, A.V. Moholkar, D. SChoi, J.H. Yun, J.H. Moon, S.S. Kolekar, J.H. Kim, Single step electrosynthesis of Cu_2ZnSnS_4 (CZTS) thin films for solar cell application, Electrochimica Acta 55 (2010) 4057–4061.
[22] X. Zhang, X. Shi, W. Ye, C. Ma, C. Wang, Electrochemical deposition of quaternary Cu_2ZnSnS_4 thin films as potential solar cell material, Appl. Phys. A Mater. Sci. Process. 94 (2009) 381–386.
[23] J.J. Scragg, P.L. Dale, L.M. Peter, Towards sustainable materials for solar energy conversion: preparation and photo-electrochemical characterization of Cu_2ZnSnS_4, Electrochem. Commun. 10 (2008) 639–642.
[24] J.J. Scragg, D.M. Berg, P.J. Dale, A 3.2% efficient kesterite device from electrodeposited stacked elemental layers, J. Electroanal. Chem. 646 (2010) 52–59.
[25] K. Tanaka, Y. Fukui, N. Moritake, H. Uchiki, Chemical composition dependence of morphological and optical properties of Cu_2ZnSnS_4 thin films deposited by sol–gel sulfurization and Cu_2ZnSnS_4 thin film solar cell efficiency, Sol. Energy Mater. Sol. Cells 95 (2011) 838–842.
[26] K. Maeda, K. Tanaka, Y. Fukui, H. Uchiki, Influence of H_2S concentration on the properties of Cu_2ZnSnS_4 thin films and solar cells prepared by sol–gel sulfurization, Sol. Energy Mater. Sol. Cells 95 (2011) 2855–2860.
[27] K. Tanaka, M. Oonuki, N. Moritake, H. Uchiki, Cu_2ZnSnS_4 thin film solar cells prepared by non-vacuum processing, Sol. Energy Mater. Sol. Cells 93 (2009) 583–587.
[28] N. Moritake, Y. Fukui, M. Oonuki, K. Tanaka, H. Uchiki, Preparation of Cu_2ZnSnS_4 thin film solar cells under non-vacuum condition, Phys. Status Solidi C 6 (2009) 1233–1236.
[29] P.K. Sarswat, M.L. Free, Demonstration of a sol–gel synthesized bifacial CZTS photoelectrochemical cell, Phys. Status Solidi A208 (2011) 2861–2864.
[30] A. Fischereder, T. Rath, W. Haas, H. Amenitsch, J. Albering, D. Meischler, S. Larissegger, M. Edler, R. Saf, F. Hofer, G. Trimmel, Investigation of Cu_2ZnSnS_4 formation from metal salts and thioacetamide, Chem. Mater. 22 (2010) 3399–3406.
[31] H. Park, Y.H. Hwang, B.S. Bae, Sol–gel processed Cu_2ZnSnS_4 thin films for a photovoltaic absorber layer without sulfurization, J. Sol–Gel Sci. Technol. 65 (2013) 23–27.
[32] K. Tanaka, N. Moritake, H. Uchiki, Preparation of Cu_2ZnSnS_4 thin films by sulfurizing sol–gel deposited precursors, Sol. Energy Mater. Sol. Cells 91 (2007) 1199–1201.
[33] M.Y. Yeh, C.C. Lee, D.S. Wuu, Influences of synthesizing temperatures on the properties of Cu_2ZnSnS_4 prepared by sol–gel spin-coated deposition, J. Sol–Gel Sci. Technol. 52 (2009) 65–68.
[34] T.K. Chaudhurin, D. Tiwari, Earth-abundant non-toxic Cu_2ZnSnS_4 thin films by direct liquid coating from metal–thiourea precursor solution, Sol. Energy Mater. Sol. Cells 101 (2012) 46–50.
[35] S. Elfarrass, B. Hartiti, A. Ridah, P. Thevenin, Effect of different S/In ratio of In_2S_3 films prepared by chemical spray pyrolysis method, J. Mater. Environ. Sci. 6 (2015) 487–490.
[36] N. Kamoun, H. Bouzouita, B. Rezig, Fabrication and characterization of Cu_2ZnSnS_4 thin films deposited by spray pyrolysis technique, Thin Solid Films. 515 (2007) 5949–5952.
[37] D.A. Luh, T. Miller, J.J. Paggel, T.C. Chiang, Large Electron-Phonon Coupling at an Interface, Phys. Rev. Lett. 88 (2002), 256802–1-256802-4.
[38] G. Taguchi, E.A. Elsayed, T. Hsaing, Quality Engineering in Production Systems, McGraw-Hill, NewYork, 1989.
[39] P.J. Ross, Taguchi Techniques for Quality Engineering: Loss Function, Orthogonal Experiments, Parameter and Tolerance Design, McGraw-Hill, New York, 1996.
[40] S.H. Park, Robust Design and Analysis for Quality Engineering, Chapman & Hall, New Jersey, 1996.
[41] S. Chen, X.G. Gong, A. Walsh, S.H. Wei, Crystal and electronic band structure of Cu_2ZnSnX_4 (X=S and Se) photovoltaic absorbers: First-principles insights, Appl. Phys. Lett. 94 (2009) 041903–041908.
[42] L.-J. Chen, Y.-J. Chuang, Quaternary semiconductor derived and formation

mechanism by non-vacuum route from solvothermal nanostructures for high-performance application, Mater. Lett. 91 (2013) 372–375.
[43] Y.M. Chiang, H.-H. Hsieh, The use of the Taguchi method with grey relational analysis to optimize the thin-film sputtering process with multiple quality characteristic in color filter manufacturing, Comput. Industrial Eng. 56 (2009) 648–661.
[44] L.-I. Tong, C.-T. Su, Optimizing multi-response problems in the Taguchi method by fuzzy multiple attribute decision making, Qual. Reliab. Int. 13 (1997) 25–34.
[45] S. Kahraman, S. Çetinkaya, M. Podlogar, S. Bernik, H.A. Çetinkara, H.S. Güder, Effects of the sulfurization temperature on sol gel-processed Cu_2ZnSnS_4 thin films, Ceram. Int. 39 (2013) 9285–9292.
[46] Y.B. Kishore Kumar, G. Suresh Babu, P. Uday Bhaskar, V. Sundara Raja, Preparation and characterization of spray-deposited Cu_2ZnSnS_4 thin films, Sol. Energy Mater. Sol. Cells 93 (2009) 1230–1237.
[47] E.K. Michael, D. Norcini, S. Komarneni, J.R.S. Brownson, Nanocomposite synthesis and characterization of Kesterite, Cu_2ZnSnS_4 (CZTS) for photovoltaic applications, Ceram. Int. 39 (2013) 7935–7941.
[48] Y. Ohta, Y. Haga, Y. Abe, Crystallographic features of ZnO single crystals, Jpn. J. Appl. Phys. 36 (1997) L1040–L1042.
[49] K. Jimbo, R. Kimura, T. Kamimura, S. Yamada, W.S. Maw, H. Araki, K. Oishi, H. Katagiri, Cu_2ZnSnS_4-type thin film solar cells using abundant materials, Thin Solid Films 515 (2007) 5997–5999.
[50] F.Y. Liu, K. Zhang, Y.Q. Lai, J. Li, Z.A. Zhang, Growth and characterization of magnetron sputtering for photovoltaic applications, Electrochem. Solid State Lett. 13 (2010) H379–H381.
[51] T. Todorov, M. Kita, J. Carda, P. Escribano, Cu_2ZnSnS_4 films deposited by a soft-chemistry method, Thin Solid Films 517 (2009) 2541–2544.