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Influence of aluminum doping in $CuInS_2$ prepared by spray pyrolysis on different substrates

N. Kamoun Allouche[a,*], N. Jebbari[a], C. Guasch[b], N. Kamoun Turki[a]

[a] Laboratoire de Physique de la Matière Condensée, Faculté des Sciences de Tunis (2092) El Manar, Tunisia
[b] Institut d'Electronique du Sud, Université Montpellier II Place Eugène Bataillon – CC082 – 34095 Montpellier, France

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ABSTRACT

The structural and optical properties of the $CuInS_2$ semiconductor thin films doped with aluminum ($[Al]/[In] = 1‰$ and 2‰) are reported. Films are deposited using the spray pyrolysis technique on various substrates: glass, In_2S_3/glass, ZnO/glass, as well as SnO_2/glass, In_2S_3 and ZnO are used as optical windows in photovoltaic system, $CuInS_2$ as the absorber material and SnO_2 as ohmic contact. In_2S_3, ZnO and SnO_2 are grown by spray pyrolysis. During $CuInS_2$ thin layer deposition, the substrate temperature is 340 °C. The deposition run lasts for 5 min.

X-ray diffraction is used to characterize $CuInS_2$ film cristallinity. The effect of aluminum inclusions as well as of the substrate material on the $CuInS_2$ film is investigated.

The optical absorption coefficient α for the Al-doped $CuInS_2$ compounds is obtained from reflection and transmission spectra. It is in the range of $[3.69–4.37] \times 10^6\ cm^{-1}$ ($[9.55–12.31] \times 10^6\ cm^{-1}$, respectively) for 1‰ aluminum content in the spray solution (2‰, respectively).

The direct band gap value is in the order of 1.44 eV for the 1‰ Al-doped $CuInS_2$ thin layers and 1.48 eV for 2‰ Al content.

1. Introduction

Photovoltaic solar cells based on I–III–VI_2 ternary chalcopyrite absorber layers, have been the focus of intense investigation for over two decades. The use of chalcopyrite absorbers is highly appealing since their band gaps coincide with the maximum photon power density in the solar spectrum. Cu-chalcopyrite semiconductors have been studied extensively in recent years due to their applications as absorbers for large-area low-cost photovoltaic devices [1]. $CuInS_2$ as a chalcopyrite nontoxic semiconductor material has a high absorption coefficient and a direct band gap varying from 1.39 to 1.55 eV depending on the method of preparation [2–7]. It is therefore, a promising candidate for photovoltaic applications. Different methods such as vacuum co-evaporation [8], electrochemical deposition [9,10], sputtering [11,12], spray pyrolysis [13–16], etc. have been used to prepare $CuInS_2$ films. Among these methods, spray pyrolysis, used in the present study, is attractive because large-area films with good uniformity may be prepared at low cost [17].

In the present work, the growth of aluminum-doped $CuInS_2$ thin films by spray pyrolysis on various substrates (glass, In_2S_3/glass, ZnO/glass, SnO_2/glass) is studied. In_2S_3, ZnO and SnO_2 were grown by spray pyrolysis [18–20]. In_2S_3 and ZnO are used as optical windows and SnO_2 as ohmic contact. The structure, phase composition and optical properties of the aluminum-doped $CuInS_2$ sprayed films are characterized.

2. Experimental procedure

$CuInS_2$ thin films are prepared by the pulverization technique in liquid phase (spray). The experimental setup used to spray $CuInS_2$ thin layers involves a heating system, for the substrate a nozzle fixed on a two-dimensional moving table allowing to pulverize the whole isothermal zone containing the heated substrates. Nitrogen is used as carrier gas. The aqueous solutions used for pulverization contain the precursors of the $CuInS_2$ material, i.e. $CuCl_2$ for the copper, $InCl_3$ for the indium and $SC(NH_2)_2$ for the sulphur. The $CuInS_2$ films are formed on heated substrates at 340 °C. During the deposition run, respectively, the rate of spray and the distance between the substrate and the nozzle are maintained constant and are equal to 5 ml/min and 25 cm. The spray run lasts for 5 min [17].

The layer structure is studied by X-ray diffraction (XRD), using an automated Bruker D8 advance X-ray diffractometer with CuKα radiations for 2θ values over 20–60°. The wavelength, the accelerating voltage and the current were 1.5418 Å, 40 kV and 20 mA, respectively. The film surface morphology is studied using a JEOL 6300F scanning electron microscopy (SEM). Auger measurements are carried out with a Riber system equipped with a cylindrical mirror analyser (CMA) and working on the first derivative mode. The optical properties are studied with a UV–VIS–NIR spectrophotometer (Cary 5000) in the wavelength range of 200–2500 nm at room temperature.

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* Corresponding author. Tel.: +216 97 660 308; fax: +216 71 885 073.
E-mail address: norhen_kamoun@yahoo.fr (N.K. Allouche).

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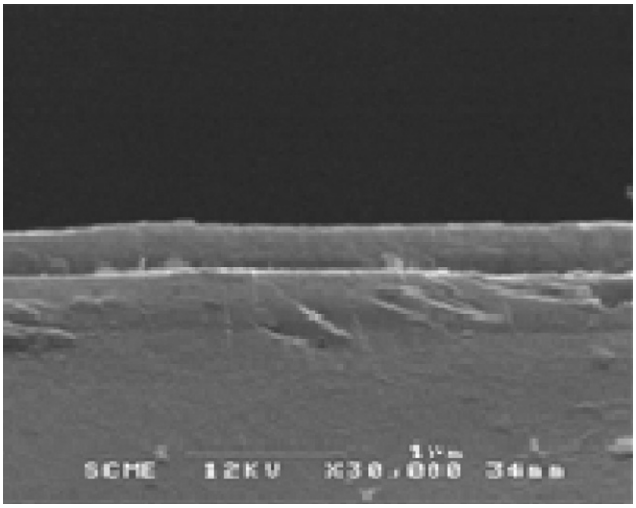

Fig. 1. SEM cross-sectional image of undoped $CuInS_2$ film grown on glass substrate showing the film thickness (0.3 μm).

3. Results and discussion

3.1. Morphological and structural properties

According to SEM study, the obtained $CuInS_2$ films are homogeneous with a good adherence to the substrate. Indeed, Fig. 1 presents the cross-sectional SEM image of a typically obtained $CuInS_2$ layer on glass without any doping of aluminum. In this image the $CuInS_2$/glass interface is clearly discernable, indicating a good microstructure of the sprayed film. The thickness of the sprayed $CuInS_2$ layers is about 0.3 μm.

Fig. 2 gives representative SEM micrographs of the $CuInS_2$ film surface for [Al]/[In] = 0‰, 1‰ and 2‰. We note that that the roughness increases with increase ratio of Al/In.

XRD spectra of $CuInS_2$ film sprayed on glass without any doping (a), doped with 1‰ (b) and with 2‰ (c) aluminum are shown in Fig. 3. A highly (1 1 2) preferential orientation is observed. The (2 2 0) and (3 1 2) diffraction peaks are also detected. Therefore, the

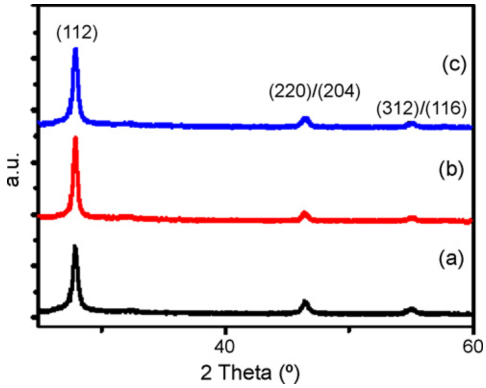

Fig. 3. X-ray diffraction spectra for Al-doped $CuInS_2$ thin film grown on glass substrate by spray pyrolysis: (a) [Al]/[In] = 0‰; (b) [Al]/[In] = 1‰; (c) [Al]/[In] = 2‰.

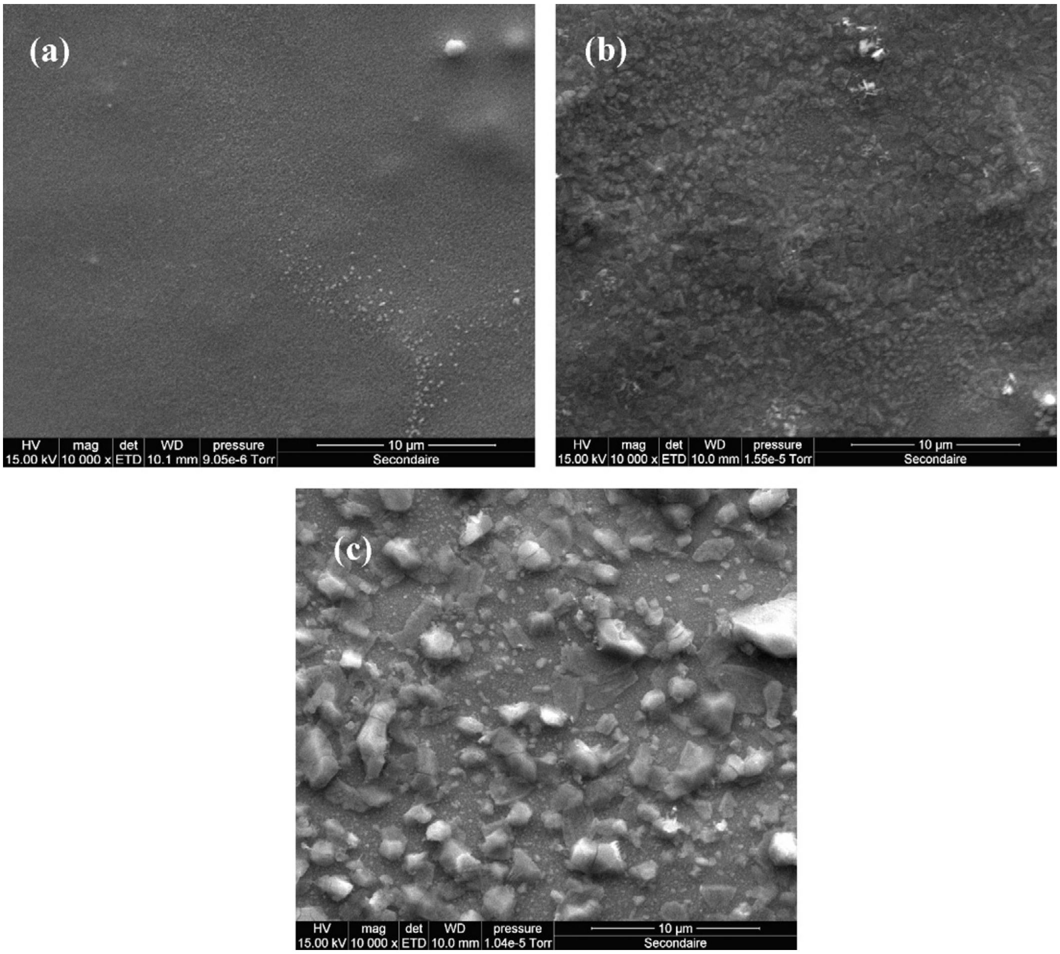

Fig. 2. SEM images for Al-doped $CuInS_2$ thin film grown on glass substrate spray pyrolysis: (a) ([Al]/[In] = 0‰); (b) ([Al]/[In] = 1‰); (c) ([Al]/[In] = 2‰).

Table 1
Analysis of surface composition of the $CuInS_2$:Al thin film by Auger electron spectroscopy.

[Al]/[In]	0‰	1‰	2‰
H(Cu)/H(In)	0.720	0.443	0.258
H(S)/H(In)	0.090	0.095	0.153
H(Cl)/H(In)	0.041	0.059	0.092
H(O)/H(In)	2.340	1.551	1.634
H(C)/H(In)	1.670	0.781	1.909

prepared $CuInS_2$ thin films exhibit the chalcopyrite structure. It may also be interesting to note that the relative intensity of the (1 1 2) diffraction peak increases by increasing the inclusion rate of aluminum.

3.2. *Auger studies*

Auger studies are useful in order to get information on the surface layer composition and to detect a possible effect of the aluminum inclusion. In this work, Auger studies are only used to obtain qualitative information on the role of the aluminum and to deduce the main features of the surface layer.

We would like to emphasize on the modification induced by the variation of the aluminum-doping rate on the sprayed $CuInS_2$ films. Indeed, we find spectra characterized by the presence of the constituent element Cu, In, and S, as well as Cl, as inert residue of the chemical spray solution. As expected, C and O are also detected, as impurity elements adsorbed in the surface layer. The oxygen may be incorporated into the film either from the atmosphere or from the aqueous solutions during the spray run. The source for carbon contamination may be due to the exposure of the samples to atmospheric air, and the laboratory environment in which samples are manipulated.

We calculate the Cu/In, S/In, Cl/In, O/In and C/In ratios for the $CuInS_2$ thin films grown with different aluminum-doping rate (Al/In = 0‰, 1‰ and 2‰). These results are reported in Table 1. It is clear that Al-doping influences surface composition of the $CuInS_2$:Al layer. As Al is incorporated in the volume Cu decreases, and S increases slightly; Cl is increased, C contamination is variable and O is reduced at the surface.

3.3. *Optical properties*

Transmission and reflection measurements at near-normal incidence are performed in order to compare the effect of the variation of aluminum inclusion rate ([Al]/[In] = 1‰ and 2‰) on the optical performances of $CuInS_2$ films deposited on various substrates (Glass, In_2S_3/glass, ZnO/glass, SnO_2/glass).

Transmission and reflection spectra are presented in Fig. 4a and b, respectively.

For the large wavelengths (λ), we notice on the transmission spectra presented in Fig. 4a that interference fringes are present only for $CuInS_2$ films deposited on glass and on ZnO/glass substrates. Transmission spectra show a broad cut-off towards large wavelengths for $CuInS_2$ deposited on SnO_2 which corresponds to the absorption edge of SnO_2 underlayer due to free carriers. The difference in the broadening of the short-wavelength intrinsic absorption edge results in a change of the substrates rather than to any changes in the $CuInS_2$ material. It can be seen also that, for $CuInS_2$ deposited on ZnO substrate, the transmission in the transparency region is larger and the short-wavelength absorption edge is sharper. Similar results are found for 2‰ aluminum inclusion rate.

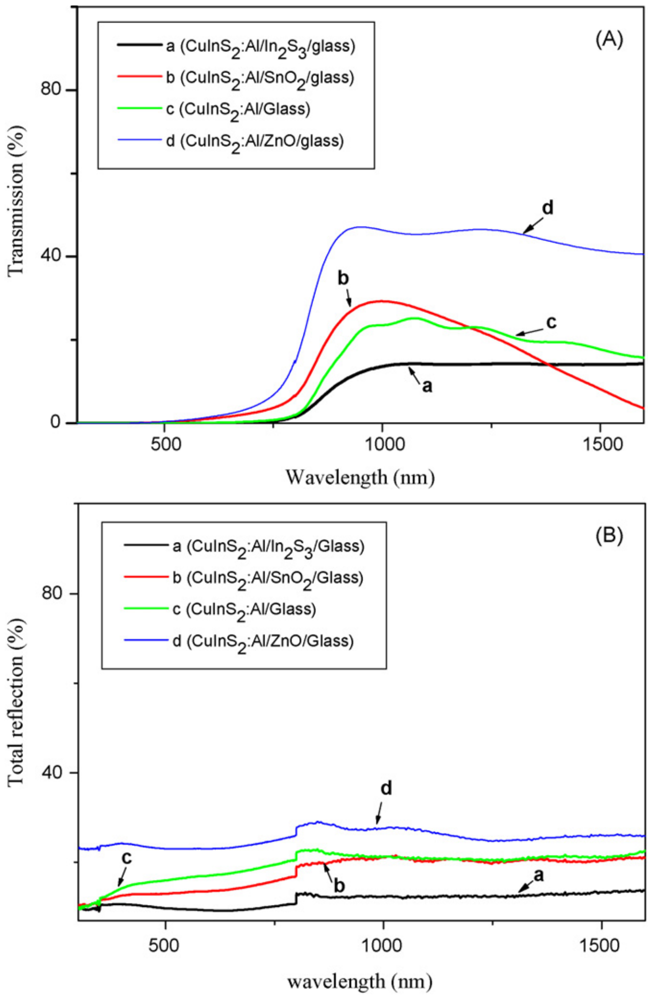

Fig. 4. Transmission (a) and reflection (b) spectra of $CuInS_2$:Al thin films sprayed on various substrates ([Al]/[In] = 1‰).

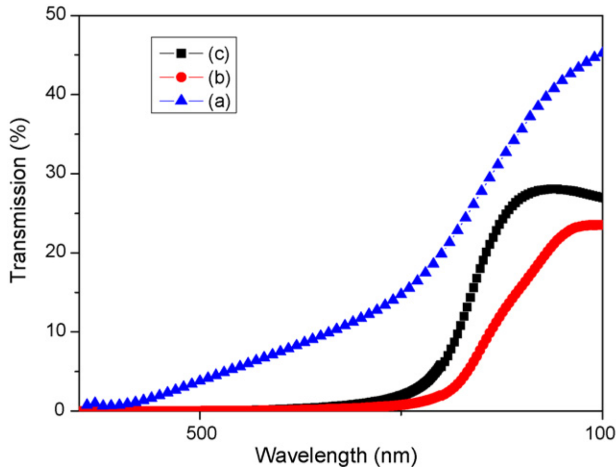

Fig. 5. Transmission spectra of $CuInS_2$:Al thin films sprayed grown on glass substrate by spray pyrolysis: (a) ([Al]/[In] = 0‰); (b) ([Al]/[In] = 1‰); (c) ([Al]/[In] = 2‰).

Fig. 5 shows the transmission (*T*) spectra of $CuInS_2$ sprayed thin films on glass substrates for [Al]/[In] = 0‰, 1‰ and 2‰. When the aluminum inclusion rate changes from 1‰ to 2‰, the intrinsic absorption edge increases as well as the transmission value over the whole spectral range. Their intrinsic absorption edge increase is explained below.

Based on the optical transmission and reflection measurements, $(\alpha h\nu)^2$ is plotted as a function of photon energy ($h\nu$) in Fig. 6 for 1‰ and 2‰ Al-doping rate. It can be seen that the films have a

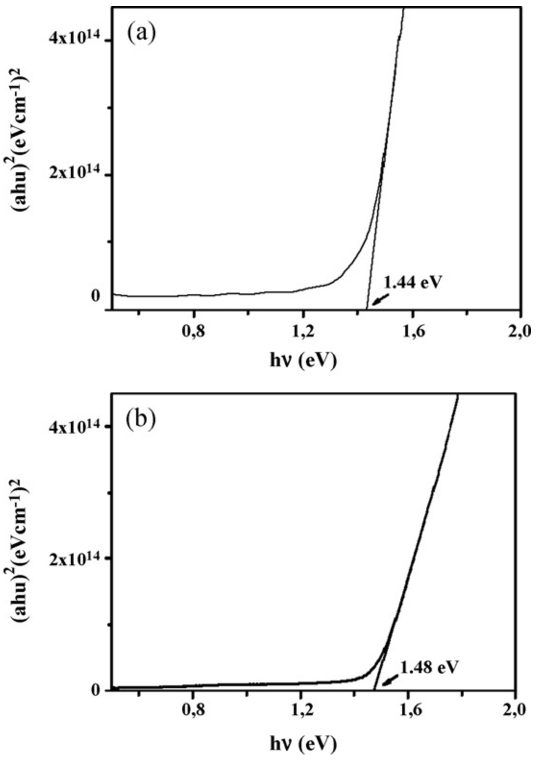

Fig. 6. $(\alpha h\nu)^2$ versus $h\nu$ plots of $CuInS_2$:Al thin films sprayed on glass: (a) ([Al]/[In] = 1‰); (b) ([Al]/[In] = 2‰).

Table 2
Band gap values of $CuInS_2$:Al thin films sprayed on various substrates ([Al]/[In] = 1‰).

Substrate deposition for $CuInS_2$:Al	In_2S_3/glass	SnO_2/glass	Glass	ZnO/glass
Band gap values (eV)	1.40	1.45	1.44	1.43

steep optical absorption feature, indicating good homogeneity in the shape and size of the grains as well as low defect density near the band edge. $(\alpha h\nu)^2$ varies almost linearly with $h\nu$ above the band gap energy (E_g). Thus, the following equation can be applied for a direct inter-band transition [21]:

$$(\alpha h\nu)^2 = A(h\nu - E_g)$$

where A is a constant.

The band gap energy is obtained by extrapolating the linear portion of the plot to the crossing with $h\nu$ axis. For undoped $CuInS_2$ thin films, E_g equals 1.39 eV [7]. Indeed, the 1‰ and 2‰ Al-doped films have band gap energy equal to 1.44 and 1.48 eV, respectively, which is in the suitable range for sunlight absorption and closely agrees with the values reported for $CuInS_2$ thin films obtained by spray chemical vapor deposition [4] and by reactive sputtering [22]. The band gap energy values of $CuInS_2$:Al thin films sprayed on various substrates ([Al]/[In] = 1‰) are reported in Table 2. E_g varies from 1.40 to 1.45 eV. The E_g variation shown in Table 2 could be explained by the change of the surface morphology.

The study of the optical properties from reflection and transmission spectra allows us to determine reliable value of the optical absorption coefficient α for the Al-doped $CuInS_2$ thin films. α is in the range of $[3.69–4.37] \times 10^6\ cm^{-1}$ and $[9.55–12.31] \times 10^6\ cm^{-1}$ for 1‰ and 2‰ aluminum contents in the spray solution of $CuInS_2$ material, respectively. Moreover, the underlying conductive layer (ZnO, In_2S_3 or SnO_2) has an effect on the optical properties of $CuInS_2$:Al thin film. Therefore, the In_2S_3 and ZnO optical windows and SnO_2 ohmic contact appear to have promising technological impact.

4. Conclusion

$CuInS_2$ thin films are prepared on various substrates by the spray technique. It is particularly observed that well crystallized $CuInS_2$ thin films are obtained with low rate (1‰ and 2‰) of aluminum inclusion. Indeed, doping the $CuInS_2$ with aluminum from 0‰ to 2‰ is related with the increasing of the (1 1 2) diffraction peak relative intensity and with the increasing of the optical band gap energy (E_g). The optical absorption coefficient α is found to increase when the aluminum inclusion rate in the $CuInS_2$ films increases. $CuInS_2$ film prepared with 2‰ aluminum doping shows a high absorption coefficient varying from 9.5 to $12.31 \times 10^6\ cm^{-1}$ and a band gap of 1.48 eV practically equal to the theoretical one of 1. eV.

From these studies we are able to optimize the process in order to produce the layer suitable for optical absorbers in solar cells.

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References

[1] S. Siebentritt, Thin Solid Films 403/404 (2002) 1.
[2] B. Tell, J.L. Shay, H.M. Kasper, Phys. Rev. B 4 (1971) 2463.
[3] J.L. Shay, J.H. Wernick, Ternary Chalcopyrite Semiconductors: Growth, in: Electronic Properties and Applications, Pergamon Press, Oxford, 1975.
[4] D.O. Henderson, R. Mu, A. Ueda, M.H. Wu, E.M. Gordon, Y.S. Tung, M. Huang, J. Keay, L.C. Feldman, J.A. Hollingsworth, W.E. Buhro, J.D. Harris, A.F. Hepp, R.P. Rafaelle, Mater. Des. 22 (2001) 585–589.
[5] J. Klaer, J. Burns, R. Henninger, K. Siemer, R. Klenk, K. Ellmer, D. Bräunig, Semicond. Sci. Technol. 13 (1998) 1456.
[6] F. Payment, Electrodéposition du semiconducteur ternaire CuInS2 pour utilization dans une cellule photovoltaique électrochimique, mémoire de maîtrise, UQAM, 2003, 134 pp.
[7] N. Kamoun, R. Bennaceur, J.M. Frigerio, J. Phys. III France 4 (1994) 983.
[8] M. Abaab, M. Kanzari, B. Rezig, M. Brunel, Sol. Energy Mater. Sol. Cells 59 (1999) 299.
[9] T. Yukawa, K. Kuwabara, K. Koumoto, Thin Solid Films 286 (1996) 151.
[10] B. Asenjo, A.M. Chaparro, M.T. Gutiérrez, J. Herrero, Thin Solid Films 511–512 (2006) 117–120.
[11] (a) T. Watanabe, M. Matsui, K. Mori, Sol. Energy Mater. Sol. Cells 35 (1994) 239; (b) Y. Yamamoto, T. Tanaka, N. Tanahashi, A. Yoshida, T. Yamaguchi, Sol. Energy Mater. Sol. Cells 49 (1997) 399.
[12] X. Ping Liu, L. Shao, Surf. Coat. Technol. 201 (2007) 5340–5343.
[13] M. Ortega-López, A. Morales-Acevedo, Thin Solid Films 330 (1998) 96.
[14] M. Krunks, O. Kijatkina, H. Rebane, I. Oja, V. Mikli, A. Mere, Thin Solid Films 403–404 (2002) 71.
[15] T.T. John, T. Sebastian, C. Sudha Kartha, K.P. Vijayakumar, T. Abe, Y. Kashiwaba, Phys. B: Condens. Matter 388 (2007) 1–9.
[16] A. Katerski, A. Mere, V. Kazlauskiene, J. Miskinis, A. Saar, L. Matisen, A. Kikas, M. Krunks, Thin Solid Films 516 (2008) 7110–7115.
[17] N. Kamoun, N. Jebbari, S. Belgacem, R. Bennaceur, J. Bonnet, F. Touhari, L. Lassabatere, J. Appl. Phys. 91 (2002).
[18] N. Kamoun, S. Belgacem, M. Amlouk, R. Bennaceur, J. Bonnet, F. Touhari, M. Nouaoura, L. Lassabatere, J. Appl. Phys. 89 (2001).
[19] M. Amlouk, F. Touhari, S. Belgacem, N. Kamoun, D. Barjon, R. Bennaceur, Phys. Status Solidi 73 (1997).
[20] S. Belgacem, R. Bennaceur, Rev. Phys. Appl. 25 (1990) 1245.
[21] H.T. Grahn, Introduction to Semiconductor Physics, World Scientific Publishing, Singapore, 1999.
[22] Y.B. He, A. Polity, H.R. Alves, I. Osterreicher, W. Kriegseis, D. Pfisterer, B.K. Meyer, M. Hardt, Thin Solid Films 403–404 (2002) 62–65.