Applied Surface Science 257 (2011) 2193–2196

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

$CuInS_2$ thin films obtained through the annealing of chemically deposited In_2S_3–CuS thin films

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ARTICLE INFO

Article history:
Received 12 February 2010
Received in revised form
14 September 2010
Accepted 18 September 2010
Available online 25 September 2010

Keywords:
$CuInS_2$
Thin Films
Chemical bath deposition

ABSTRACT

In this work, we report the formation of $CuInS_2$ thin films on glass substrates by heating chemically deposited multilayers of copper sulfide (CuS) and indium sulfide (In_2S_3) at 300 and 350 °C in nitrogen atmosphere at 10 Torr. CIS thin films were prepared by varying the CuS layer thickness in the multilayers with indium sulfide. The XRD analysis showed that the crystallographic structure of the $CuInS_2$ (JCPDS 27-0159) is present on the deposited films. From the optical analysis it was estimated the band gap value for the CIS film (1.49 eV). The electrical conductivity varies from 3×10^{-8} to $3\,\Omega^{-1}\,cm^{-1}$ depending on the thickness of the CuS film. CIS films showed p-type conductivity.

1. Introduction

Copper indium sulfide ($CuInS_2$) thin films are one of the most promising absorber materials in solar cells because of its high optical absorption coefficient ($10^5\,cm^{-1}$), and optimum optical band gap of 1.5 eV. This material has been incorporated in photovoltaic structures resulting in considerable conversion efficiencies [1,2]. Scheer et al. [1] showed an efficiency of 10.2% using $CuInS_2$, the device was prepared by depositing a cadmium sulfide layer as window material. Ellmer et al. [2] prepared $CuInS_2$ absorbers for thin film solar cells by using the reactive magnetron sputtering technique. After the first experiments a solar cell efficiency of 6.4% at AM1.5 was achieved.

Some authors have used the chemical bath deposition technique to deposit $CuInS_2$ thin films. Pathan and Lokhande [3] obtained CIS thin films by chemical method, the electrical resistivity of the films was of the order of 10 Ω cm, and showed p-type electrical conductivity. On the other hand, some authors have preferred other routes to grow CIS thin films, some of these are: spray pyrolysis [4,5], sputtering [6], one-stage RF reactive sputtering [7] and chemical bath deposition [8,9].

The main purpose of the present work is to deposit good quality CIS thin films using simple chemical bath deposition method. In this paper we report the results of $CuInS_2$ thin films through a process of multilayers deposited from indium sulfide (In_2S_3) and copper sulfide (CuS) films. These multilayers were annealed in nitrogen atmosphere.

2. Experimental details

2.1. Deposition of indium sulfide thin films

Chemically deposited indium sulfide thin films were obtained by following the procedure given in Ref. [10] using indium chloride (InCl3, 99.99% Alfa Aesar) and thioacetamide (CH_3CSNH_2, 99.8%, Fisher Chemical) as precursor materials. The chemical bath was prepared as follows: 10 ml of $InCl_3$ 0.1 M, 20 ml of acetic acid 0.5 M (99.9% CTR Scientific) and 20 ml of thioacetamide 1 M was mixed and diluted to 100 ml with distilled water, the reagents were mixed by stirring. The glass substrates (Corning, 25 mm × 75 mm) were placed vertically in the solution at 25 °C for 60 h without stirring. The films obtained have a thickness of 0.3 μm.

2.2. Deposition of CuS thin films

The procedure given in Ref. [11] was followed to deposit copper sulfide thin films by using 5 ml of 0.5 M solution of $CuCl_2{\cdot}2H_2O$ (99%, Fisher Chemicals) mixed with 9 ml of 1 M solution of $Na_2S_2O_3$ (99.7%, Fermont), 10 ml of 0.5 M dimethylthiourea (99%, Aldrich), and the remainder with distilled water to complete 100 ml, the reagents were mixed by stirring. Indium sulfide thin films (0.3 μm) were used as substrates, and for the deposition the substrates were placed vertically in the solution at 70 °C for 1, 2, and 2.5 h without stirring. Multilayer films In_2S_3–CuS were deposited on both

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doi:10.1016/j.apsusc.2010.09.071

sides of the substrates. The thin film deposited on the side of the substrate facing the beaker wall was retained for the optical and electrical characterization. The coating on the other side was wiped off with dilute hydrochloric acid (HCl). The thickness obtained for films deposited for 1, 2 and 2.5 h was 0.22, 0.28, and 0.35 μm, respectively.

The multilayer films were annealed at 300 and 350 °C in nitrogen atmosphere for 30 min at 10 Torr to form the crystalline phase of $CuInS_2$.

2.3. Characterization

XRD diffraction patterns were recorded on a Siemens D-500 X-ray diffractometer using Cu K_α radiation (λ = 1.5406 Å). Atomic force microscopy (AFM) analysis was done using JEOL Model JSPM-4210 equipment, the topography contrast images were acquired in the no contact mode. The optical transmittance at normal incidence spectra of the samples were measured with a spectrophotometer UV-3101PC region 1100–190 nm wavelength range. For the electrical measurements current versus time data were recorded on a computerized system using a Keithley 6487 programmable voltage source. Pairs of coplanar silver print electrodes of 5 mm length at 5 mm separation were painted on the surface of the films. The samples were illuminated with a tungsten-halogen lamp, which provided an intensity of illumination of 350 W/m^2 at the plane of the sample. Current in the dark was recorded for 20 s followed by 20 s under illumination, and finally 20 s in the dark. Thickness of the films was measured using an Alpha Step model 100 profilometer from Tencor Instruments.

3. Results and discussion

3.1. Structural studies

Fig. 1 shows the X-ray diffraction (XRD) patterns of In_2S_3–CuS thin film of 0.22 μm, recorded after the films were annealed in N_2 at (a) 300 °C and (b) 350 °C for 30 min at 10 Torr. The XRD pattern shown in Fig. 1(a) corresponds to $CuInS_2$ (112), but also one additional peak due to an excess of sulfur (0 8 0) was identified. Fig. 1(b) shows the XRD pattern corresponding to $CuInS_2$ (1 1 2), and additional peaks (2 2 0) and (3 1 2) corresponding to $CuInS_2$ were identified.

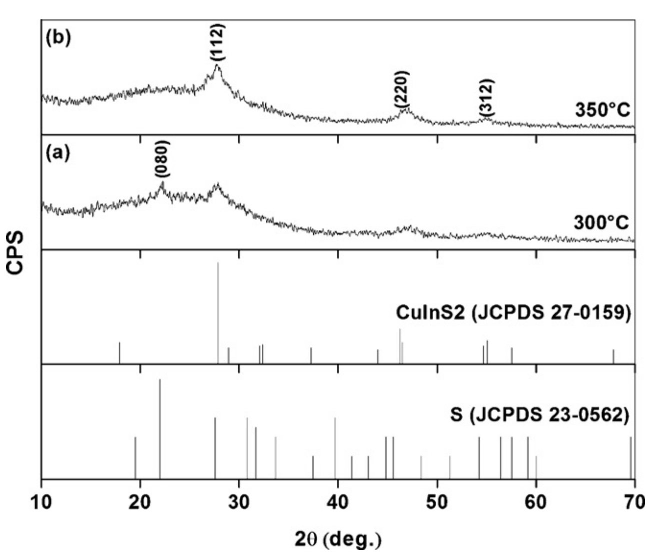

Fig. 1. XRD patterns for $CuInS_2$ (In_2S_3–CuS 0.22 μm) films: (a) after annealing in nitrogen performed for 30 min at 300 °C and 10 Torr, and (b) after annealing in nitrogen performed for 30 min at 350 °C and 10 Torr.

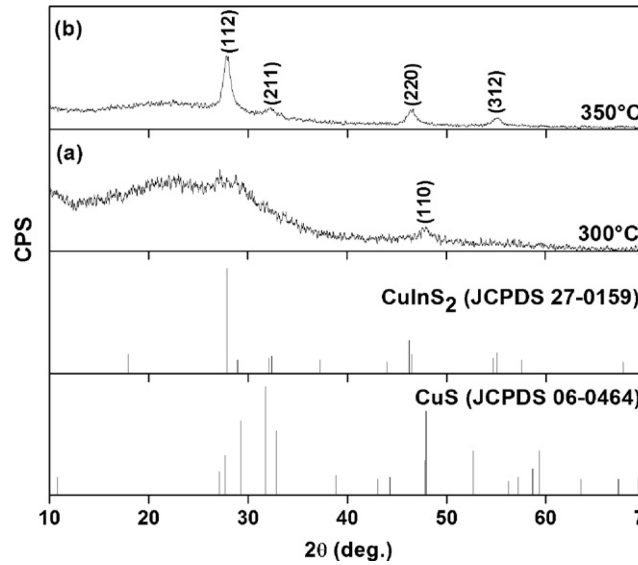

Fig. 2. XRD patterns for $CuInS_2$ (In_2S_3–CuS 0.28 μm) films: (a) after annealing in nitrogen performed for 30 min at 300 °C and 10 Torr, and (b) after annealing in nitrogen performed for 30 min at 350 °C and 10 Torr.

Fig. 2 shows the X-ray diffraction (XRD) patterns of In_2S_3–CuS thin film of 0.28 μm, recorded after the films were annealed in N_2 at (a) 300 °C and (b) 350 °C for 30 min at 10 Torr. In Fig. 2(a) there are not peaks corresponding to the $CuInS_2$ compound, but there is a small peak (1 1 0) corresponding to the covellite phase (JCPDS 06-0464). Fig. 2(b) shows the XRD pattern corresponding to $CuInS_2$ (1 1 2), (2 1 1), (2 2 0), and (3 1 2).

Fig. 3 shows the X-ray diffraction (XRD) patterns of In_2S_3–CuS thin film of 0.35 μm, recorded after the films were annealed in N_2 at (a) 300 °C and (b) 350 °C for 30 min at 10 Torr. The XRD pattern shown in Fig. 3(a) corresponds to a mixture of phases: CuS (1 1 0) and (1 0 2), and $CuInS_2$ (1 1 2) and (0 0 4). Fig. 3(b) shows the XRD pattern corresponding to $CuInS_2$, there is an intense peak (1 1 2) at $2\theta = 27.8°$ and other prominent peaks (2 0 4) at 46.5° and (3 1 2)

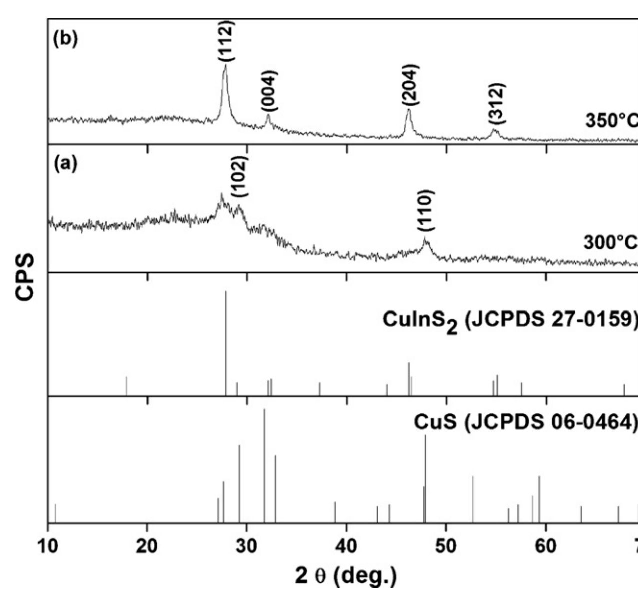

Fig. 3. XRD patterns for $CuInS_2$ (In_2S_3–CuS 0.35 μm) films: (a) after annealing in nitrogen performed for 30 min at 300 °C and 10 Torr, and (b) after annealing in nitrogen performed for 30 min at 350 °C and 10 Torr.

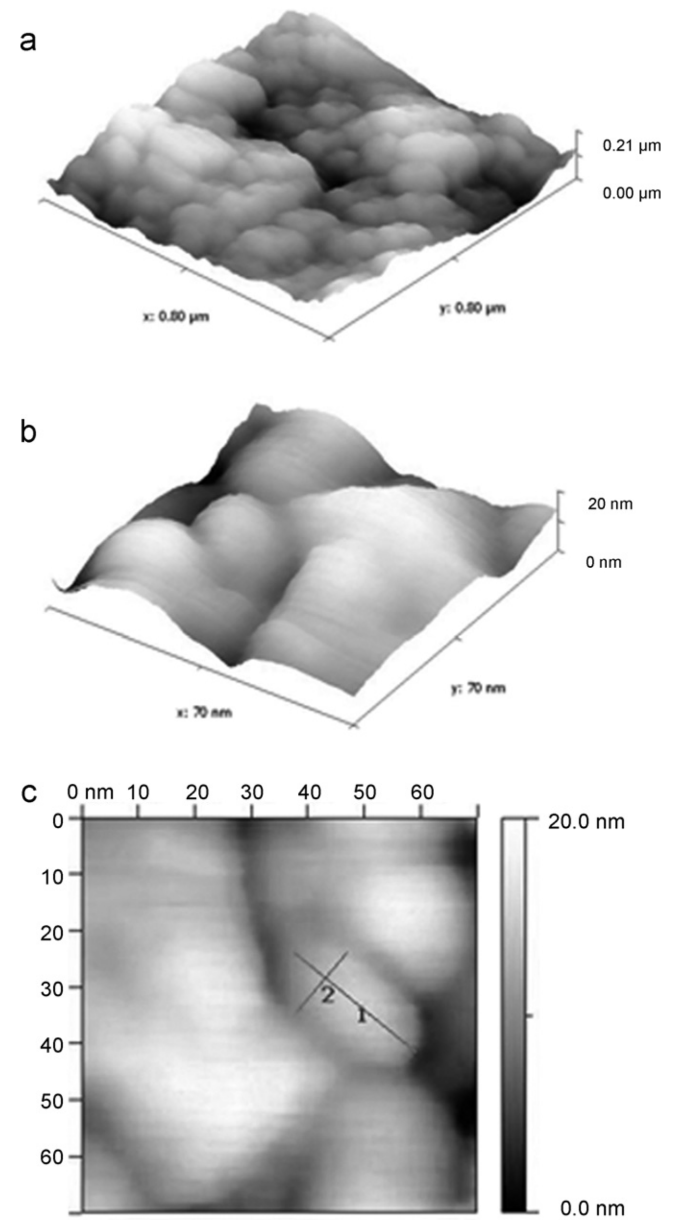

Fig. 4. AFM images of $CuInS_2$ (In_2S_3–CuS 0.35 μm) films obtained at 350 °C for 30 min, 10 Torr, (a) low magnifications, (b) high magnification, and (c) elipsoidal nanoparticle with 28 nm of major axis (line 1) and 14 nm of minor axis (line 2).

at 54.8°, which are signatures of the chalcopyrite structure of CIS. The planes (1 1 2) and (2 0 4) of the $CuInS_2$ compound were used to estimate the grain size (11 nm).

3.2. Morphological analysis

Fig. 4 shows typical AFM images of the surface topography for the $CuInS_2$ thin film (In_2S_3–CuS 0.35 μm) after annealing in nitrogen for 30 min at 350 °C, showing that the small grains had coalesced because of the annealing temperature, resulting in a uniform surface with some additional big grains observed on the film surface. Fig. 4(a) shows agglomerates of approximately 100–150 nm and a homogenous deposit on the substrate surface. The root mean square (rms) value for films is 6.3 nm. Individual nanometric particles were also observed (see Fig. 4(b)). The $CuInS_2$ film possesses ellipsoid nanoparticles with dimensions approaching 28 nm of mayor axis and 14 nm of minor axis (Fig. 4(c), line 1 and 2, respectively). This is in good agreement with the particle size estimated by X-ray diffraction (11 nm).

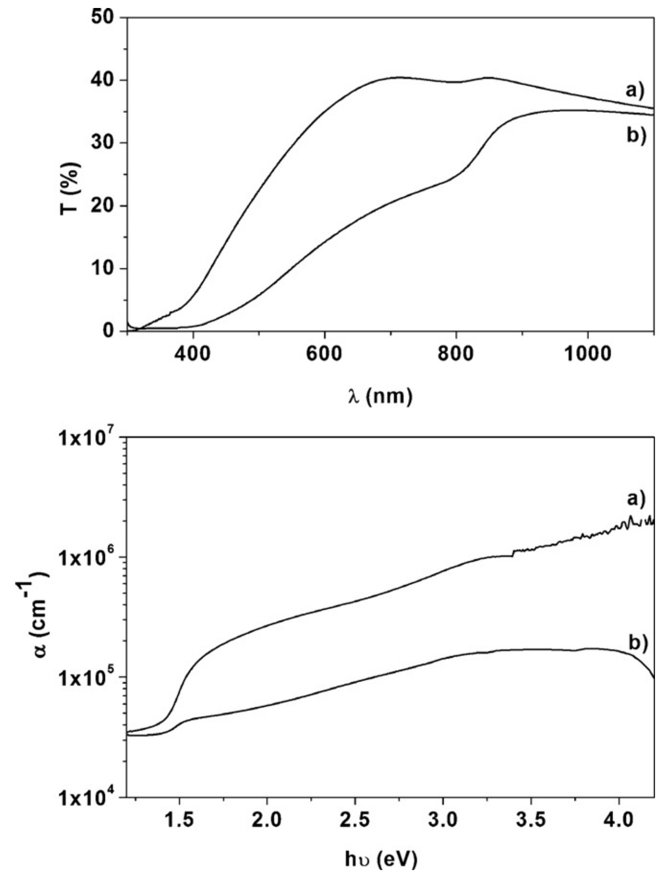

Fig. 5. Transmittance spectra and absorption coefficient for the $CuInS_2$ (In_2S_3–CuS) films: (a) 0.28 μm and (b) 0.35 μm, after annealing in nitrogen performed for 30 min at 350 °C.

3.3. Optical characterization

Fig. 5 shows the optical transmittance spectra and absorption coefficient for the $CuInS_2$ (In_2S_3–CuS) films: (a) 0.28 μm and (b) 0.35 μm, after annealing in nitrogen performed for 30 min at 350 °C. As we can see, the behavior of the transmittance spectra is different for films with different thickness of the CuS thin film. There is a shift in the absorption edge towards higher wavelengths for the thicker film. The band gap was calculated using the relationship:

$$\alpha h\nu = A(h\nu - E_g)^n \quad (1)$$

where A is a constant as a function of the transition probability and E_g is the optical band gap. The E_g values can be obtained from the best linear approximation of $(\alpha h\nu)^2$ versus $h\nu$ plot, and its extrapolation to $(\alpha h\nu)^2 = 0$ (see Fig. 6). The E_g values obtained for the $CuInS_2$ (In_2S_3–CuS 0.35 μm) films after annealing in nitrogen at 300 and 350 °C for 30 min were 1.85 eV and 1.49 eV, respectively. The E_g value of 1.49 eV for the $CuInS_2$ film obtained at 350 °C is close to the value reported for this material [12].

3.4. Electrical characterization

The electrical conductivity values obtained for $CuInS_2$ (In_2S_3–CuS: 0.22, 0.28, and 0.35 μm) films after annealing in nitrogen at 350 °C were: $10^{-8}\ \Omega^{-1}\ cm^{-1}$ (0.22 μm), $10^{-5}\ \Omega^{-1}\ cm^{-1}$ (0.28 μm), and $3\ \Omega^{-1}\ cm^{-1}$ (0.35 μm). $CuInS_2$ thin films showed p-type electrical conductivity.

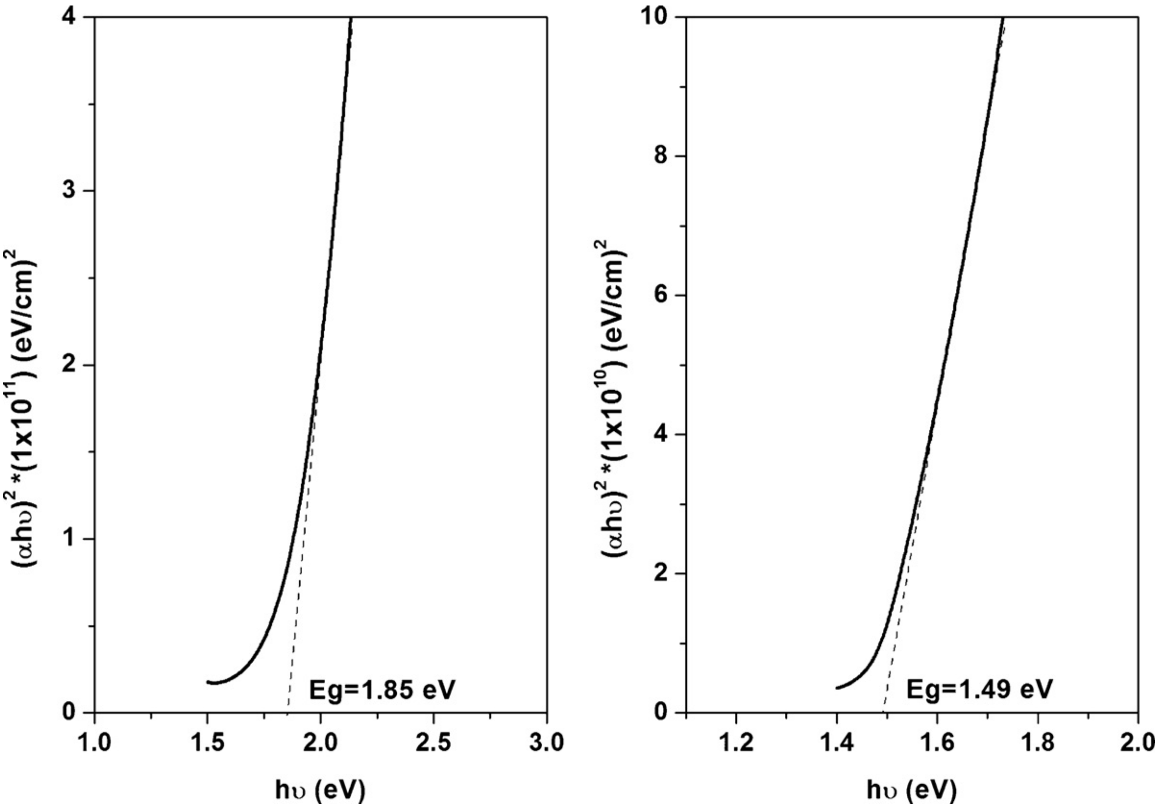

Fig. 6. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for the $CuInS_2$ (In_2S_3–CuS 0.35 μm) films after annealing in nitrogen at 300 °C (E_g = 1.85 eV) and 350 °C (E_g = 1.49 eV) for 30 min.

4. Conclusions

$CuInS_2$ thin films can be prepared by annealing chemically deposited In_2S_3–CuS thin films at 350 °C in nitrogen atmosphere for 30 min. The AFM analysis revealed that these films have a homogeneous surface and grain sizes in the order of nanometers. The conductivity values for the films vary from 10^{-8} to $3\,\Omega^{-1}\,cm^{-1}$, depending on the CuS film thickness in the multilayers. The optical band gap of 1.49 eV obtained for the $CuInS_2$ (In_2S_3–CuS, 0.35 μm) film suggests the use of this film in photovoltaic structures.

Acknowledgements

We are grateful to Maria Luisa Ramón for the XRD measurements (CIE-UNAM), José Ortega for technical support (CIE-UNAM), Dra. M.T.S. Nair and Dr. P.K. Nair (CIE-UNAM) for providing some experimental facilities. This research was supported by CONACyT (79179) and PROMEP/103.5/09/6639.

References

[1] R. Scheer, T. Walter, H.W. Schock, M.L. Fearheiley, H.J. Lewerenz, App. Phys. Lett. 63 (1993) 3294.
[2] K. Ellmer, J. Ines, J. Klaer, Thin Solid Films 413 (2002) 92.
[3] H.M. Pathan, C.D. Lokhande, Appl. Surf. Sci. 239 (2004) 11–18.
[4] M. Sahal, B. Mari, M. Mollar, Thin Solid Films 517 (2009) 2202–2204.
[5] M. Krunks, O. Kijatkina, H. Rebane, I. Oja, V. Mikli, A. Mere, Thin Solid Films 403–404 (2002) 71–75.
[6] Y. Yamamoto, T. Yamaguchi, T. Tanaka, N. Tanahashi, A. Yoshida, Solar Energy Mater. Solar Cells 49 (1997) 399–405.
[7] Y.B. He, T. Krämer, A. Polity, M. Hardt, B.K. Meyer, Thin Solid Films 431 (2003) 126–130.
[8] S. Bini, K. Bindu, M. Lakshmi, C. Sudha Kartha, K.P. Vijayakumar, Y. Kashiwaba, T. Abe, Renew. Energy 20 (2000) 405–413.
[9] F. Cui, L. Wang, Z. Xi, Y. Sun, D. Yang, J. Mater. Sci.: Mater. Electron. 20 (2009) 609–613.
[10] M.G. Sandoval-Paz, M. Sotelo-Lerma, J.J. Valenzuela-Jauregui, M. Flores-Acosta, R. Ramirez-Bon, Thin Solid Films 472 (2005) 5–10.
[11] M.T.S. Nair, L. Guerrero, P.K. Nair, Semicond. Sci. Technol. 13 (1998) 1164–1169.
[12] Y. Shi, Z. Jin, C. Li, H. An, J. Qiu, Appl. Surf. Sci. 252 (2006) 3737–3743.