Deposition time and annealing effects on morphological and optical properties of ZnS thin films prepared by chemical bath deposition

N. CHABOU^{1,*}, B. BIROUK¹, M.S. AIDA², J.P. RASKIN³

¹Renewable Energies Laboratory (LER)/ Jijel University, Algeria

²Thin Films and Interfaces Laboratory, Constantine University, Algeria

³ICTEAM/ Université Catholique de Louvain (UCL), Louvain-La-Neuve, Belgium

Nanocrystalline zinc sulfide (ZnS) thin films are prepared on glass substrates by chemical bath deposition (CBD) method using aqueous solutions of zinc chloride, thiourea ammonium hydroxide along with non-toxic complexing agent tri-sodium citrate in alkaline medium at 80 °C. The deposition time and annealing effects on the optical and morphological properties are studied. The morphological, compositional, and optical properties of the films are investigated by scanning electron microscopy (SEM), X-ray energy dispersive spectroscopy (EDAX) and UV-Vis spectroscopy. SEM micrographs exhibit uniform surface coverage. UV-Vis (300 nm to 800 nm) spectrophotometric measurements show transparency of the films (transmittance ranging from 69 % to 81 %), with a direct allowed energy band gap in the range of 3.87 eV to 4.03 eV. After thermal annealing at 500 °C for 120 min, the transmittance increases up to 87 %.

Keywords: CBD; ZnS; complexing agent; stirring; annealing

1. Introduction

The development of materials in the form of thin layers is of major interest in a wide range of applications. These thin layers have, in particular, different physicochemical properties from those of bulk materials. Metals chalcogenides are semiconductors which have attracted a lot of attention last years because of their remarkable physical properties in optoelectronic applications as well as in solar cells fabrication as a buffer layer. Nowadays, zinc sulfide is the most frequently used among these materials. ZnS has a large direct band gap (3.65 eV to 3.7 eV), high refractive index (2.25 to 2.35), and great exciton binding energy of 40 meV with n-type electrical conductivity. It is considered as one of the most suitable candidates for field emitters [1], and field effect transistors (FETs) [2]; an ideal object for fabrication of high-performance sensors and of great importance for applications in infrared windows [3] and lasers [4]. ZnS thin films

have been found valuable as buffer layer in replacement of the harmful CdS in CIGS thin film solar cells.

Different techniques can be used to deposit such a material in a thin film form, which originate from purely physical or purely chemical processes such as close-spaced vacuum sublimation technique (CSVS) [5], pulse plating [6], thermal evaporation [7], successive ionic layer adsorption and reaction (SILAR) [8], RF magnetron sputtering [9], chemical vapor deposition (CVD) [10], electrodeposition [11], spray pyrolysis [12], and flash evaporation technique [13]. The physical properties of the material are strongly dependent on the methods of preparation. We have chosen the method called CBD as this technique is relatively simple, economical and cost effective, and it can be carried out at lower temperature and pressure. The deposited layer is easily coated over large surfaces. Also this method allows us to deposit optically smooth, uniform and homogeneous layers. Chemical bath deposition was used to deposit ZnS semiconductors [14]. The quality of the deposited film

*E-mail: chabounawel@yahoo.fr

depends on the bath parameters, such as temperature, time of deposition, concentration of the reactants and the pH of the chemical bath. Recently, thin film solar cells based on chemical bath deposition of ZnS (O,OH) buffer layer have achieved an efficiency of 18.6 % [15].

In this work, ZnS thin films were deposited by the chemical bath deposition technique. The thin films were prepared from zinc chloride ZnCl_2 , thiourea ($\text{SC}(\text{NH}_2)_2$) and ammonium hydroxide (NH_4OH).

We then studied the effect of the deposition time and annealing on the growth and properties of CBD ZnS films. The typical feature of this method of deposition is the use of trisodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$) as a second complexing agent to deposit ZnS thin films in aqueous alkaline baths without stirring the reaction bath. The Na_3 -citrate is the strongest complexing agent among non-toxic complexing agents.

The films were characterized for their structural, morphological and optical properties using X-ray diffraction, scanning electron microscopy and optical absorption studies.

2. Experimental

2.1. Reaction mechanism

The CBD process enables the deposition of thin films on substrates submerged in solutions containing chalcogenide source, metal ions, and chelating agent. The latter is used to limit the hydrolysis of the metal ion and impart some stability to the bath. The deposition rate may be controlled by adjusting temperature of the bath, pH, stirring rate and relative concentration of the reactants within the solution (chalcogenide source, chelating agent and/or metal ions). Formation of ZnS film takes place when the ionic product of Zn^{2+} and S^{2-} ions exceeds the solubility product of ZnS. ZnS thin film deposition is based on the slow release of Zn^{2+} and S^{2-} ions in chemical solutions which then condense on the glass substrate.

In water solution, zinc chloride (ZnCl_2) dissolves and gives Zn^{2+} ion. Also, in alkaline medium, thiourea releases S^{2-} ions. Ammonia re-

acts with water and gives OH^- ions. These OH^- ions form the complex $\text{Zn}(\text{NH}_3)_4^{2+}$ with Zn^{2+} . Therefore, suitable complexing agents should be used to limit the free Zn^{2+} concentration and decrease the formation of zinc hydroxide and finally zinc oxide.

The various reactions involved in the ZnS growth process can be explained by the following equations:

1 – Stirrer, 2 – Hot plate, 3 – Thermocouple, 4 – Substrate, and 5 – Reactive aqueous solution

Fig. 1. Experimental setup for chemical bath deposition of thin film.

2.2. Deposition of ZnS thin films

ZnS thin films were deposited on glass substrates by CBD technique. First of all, the substrate was cleaned in deionized (DI) water, then cleaned with methanol and acetone, again rinsed in distilled water and dried in air. The degreased substrate uses nucleation centers for the growth of the films thus giving highly adhesive and uniform films. The ZnS

thin films were chemically grown on glass substrates using zinc chloride (ZnCl_2) as Zn^{2+} ion source, thiourea $\text{SC}(\text{NH}_2)_2$ as S^{2-} ion source and ammonium hydroxide (NH_4OH) and trisodium citrate as complexing agent limiting the concentration of Zn^{2+} and soluble species of Zn^{2+} in an aqueous medium.

In the first step, 20 ml of 0.1 M ZnCl_2 and 40 ml 0.6 M solution of trisodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$) were mixed and stirred for 30 min. Then, 20 ml of 0.8 M solution of thiourea were added slowly to the mixed solution under stirring condition. Then, to obtain the $\text{pH} = 11$, a sufficient amount of ammonia was added to the solution. Deionized water was added to obtain the total volume of the solution of 100 ml. The agitation was stopped. Thereafter, the glass substrates were immersed vertically inside a beaker. All reagents were of high analytical grade. Fig. 1 shows the experimental setup for chemical bath deposition technique.

The deposited film was prepared at water bath temperature $T_b = 80^\circ\text{C}$, for different durations (30 min, 60 min, 90 min, and 120 min). When the deposition reactions were completed, each sample was removed from the beaker and cleaned with deionized water and dried in air to remove the loosely adhering ZnS particles on the films. The deposit obtained was in the form of a whitish, uniform, transparent, and well adherent film. Then, the ZnS film prepared at 80°C for 90 min was annealed at 500°C for 2 hours after deposition.

The transmittance spectrum of ZnS thin film was recorded by UV-Vis (Shimadzu UV-3101) spectrophotometer in the range of 300 nm to 800 nm. The X-ray diffraction (XRD) patterns of the film were recorded using the PHILIPS PW 3710 diffractometer operating at 40 kV, 20 mA and $\lambda_{\text{CuK}\alpha} = 1.54 \text{ \AA}$. The surface morphology of the films was measured by scanning electron microscopy (SEM). Infrared spectrum of the film deposited on silicon substrate was recorded using Fourier transform infrared spectrophotometer and the composition of the film was obtained by energy-dispersive X-ray spectroscopy.

3. Results and discussion

3.1. Thin films growth

In order to explain the influence of deposition time on the formation of ZnS films, the films were deposited at various deposition times namely 60 min, 90 min, 120 min and 150 min. The variation of ZnS film deposition rate as a function of time is shown in Fig. 2. It seems clear that the deposition rate depends on deposition time. At the beginning of the deposition process, the rate of growth is decreasing as a function of time; it is high at the beginning of the deposition process due to high number of nucleation centers and becomes progressively lower thereafter. Heating of the solution reduces the concentration of NH_3 , therefore, NH_3 does not react completely with Zn^{2+} ions, and there are free Zn^{2+} ions in the reaction bath, where $\text{Zn}(\text{OH})_2$ can be easily precipitated in the basic solution causing a reduction of formation rate of ZnS. Relatively low concentration of ZnS ions in the bath results in a low growth rate. On the other hand, from a certain deposition time, the thickness increases rapidly, leading to an increase in the growth rate of the films. The time of changing of behavior is equal to 90 min. This increase can be explained by the contribution of the homogeneous regime (appearance of the particles in the solution). This regime induces an increase in the growth rate of ZnS in thin layer by the direct adsorption of the ZnS clusters found in the solution.

In Fig. 2, the ZnS film prepared at 80°C for 150 min attains a maximum film growth rate (about 4.08 nm/min).

3.2. Structural properties

The X-ray diffraction patterns (XRD) were analyzed to obtain structural information about the thin films. Fig. 3 shows the XRD patterns for a ZnS film deposited at 80°C for 90 min, obtained by scanning in 2θ range of 20° to 60° , with a grazing angle of 0.3° . The four distinguished peaks at the angles of 28.60° , 33.7° , 47.8° and 56.45° reveal a cubic lattice structure and can be assigned to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) planes, respectively [16]. These peaks were identified

Fig. 2. Deposition rate of ZnS thin films at different deposition times.

by comparing the d-spacing values obtained from the XRD patterns with JCPDS Card No. 00-065-0309 data for ZnS [17]. The (2 0 0) plane seems to be dominant. Similar (2 0 0) plane dominance was also reported for ZnS films prepared by cathodic electrodeposition technique [19].

Fig. 3. XRD spectra for as-grown CBD-ZnS thin film deposited on n-Si substrate. (◇ – ZnS; ◆ – n-Si).

3.3. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a suitable technique to study the microstructure of thin films. This technique allows us to specify the mode of growth via the study of surface roughness and to

Table 1. Mean ZnS grains size as a function of deposition time deduced from SEM images.

SEM image	Deposition time [min]	Grain size [nm]
4a	60	10
4c	90	17
4e	120	22
4g	150	20

determine the effect of different deposition times on the film morphology.

Fig. 4 shows the surface morphology of ZnS thin films deposited at temperature of 80 °C, at different deposition times, observed by SEM. From the micrographs, it is observed that the as-deposited films have uniform morphology with good surface coverage on the substrate (ion-by-ion mechanism) over which freely adhering clusters of grains (cluster-by-cluster mechanism) exist. The ZnS thin films indicate a surface structure consisting of various small particles free of pinholes. When the deposition time increases, the particle size increases from around 10 nm to 20 nm. We can conclude that the homogeneity, grain size and adhesion to the substrate can be increased by the deposition time.

We have observed from the SEM images that the grain size of the films, as a function of deposition time, evolves like in Table 1.

Chemical composition of ZnS thin films on glass substrate was analyzed by energy-dispersive X-ray analyzer (EDX) (Fig. 5). The EDX analysis confirms the presence of zinc and sulfur in the ZnS thin films. We see that the percentage of sulfur is low in the film and it is probably due to the volatility of sulfur.

Excess of Zn may be caused by $\text{Zn}(\text{OH})_2$ or ZnO originating from the alkaline reaction solution [18]. In the analysis, the presence of the peaks of O, Si, Mg, Cl and Na can be attributed to the amorphous nature of the glass substrate.

In [19] it has been suggested that oxygen atoms in the ZnS film deposited by CBD method may come from the compounds of ZnO and $\text{Zn}(\text{OH})_2$.

Fig. 4. SEM images of ZnS thin films deposited at various periods of time: (a) 60 min, (c) 90 min, (e) 120 min, (g) 150 min; (b), (d), (f), (h) – high magnifications images of (a), (c), (e), (g).

3.4. Optical properties

The optical properties of ZnS thin films were determined from the variation of the optical transmission with UV-Vis light wavelength λ ranging from 300 nm to 800 nm.

Transmittance

Fig. 6 shows the optical transmission spectra of ZnS thin films obtained in different deposition times, before and after annealing at 500 °C for 2 hours.

Fig. 5. EDX scanning pattern of the ZnS deposited at 80 °C for 60 min.

Fig. 6. Transmittance spectra of the ZnS films grown on glass substrate in various deposition times: (a) as-deposited, (b) annealed at 500 °C for 2 h.

It is clear that the transmittance decreases with the increase of deposition time, before as well as after annealing. This decrease in transmittance can be explained by the evolution of the thickness; in other words increasing the deposition time leads to thicker films. It has been observed that the films have a maximum transmittance of 81.7 % in the visible region for as-deposited films. This high transparency in the visible region indicates that there are no colloid particles formed by homogeneous reaction on the substrate surface. This result is in agreement with SEM micrographs. The average transmittance in the visible range of the film deposited for 90 min is about 87.4 %, which is higher than of that deposited at 150 min. Annealing process of the as-deposited films increases the optical transmittance. This increase may be attributed to the rearrangement and decrease of the films defects.

Absorbance and reflectance

Fig. 7 and Fig. 8 show the spectral variations of reflectance and absorbance for as-deposited and annealed films. It can be seen that all the samples of ZnS films exhibit high absorbance in UV regions. In the visible region, the absorption

is significantly lower. Also, the values for the annealed film are lower compared with the others because the annealed film has a higher transmission values.

Fig. 7. Optical absorbance of nanocrystalline ZnS thin films obtained in different deposition times versus wavelength before and after annealing.

Fig. 8. Optical reflectance of nanocrystalline ZnS thin films obtained in different deposition times versus wavelength before and after annealing.

Absorption coefficient and optical band gap

The α coefficients for as-deposited and annealed ZnS films have been calculated by the following relationship:

$$\alpha = 2.3026 A/t \quad (5)$$

where A is the absorbance and t is the sample thickness.

In Fig. 9, the variation of α versus wavelength for ZnS nanocrystalline thin layers with deposition time as parameter is reported. One can clearly see that the absorption coefficient of ZnS films increases with the decrease of wavelength.

Fig. 9. Absorption coefficient of ZnS thin films obtained in different deposition times versus wavelength before and after annealing.

The absorption coefficient values have been used to determine the optical energy gap by using the Tauc relationship which is given by the formula:

$$\alpha h\nu = \beta(h\nu - E_g)^n \quad (6)$$

in which, $h\nu$ is the photon energy, E_g is the optical band gap of the semiconductor, β is a constant and $n = 1/2$ for direct band gap semiconductor such as ZnS.

The optical band gap value of the ZnS thin films was estimated by extrapolation of the straight line of the plot of $(\alpha h\nu)^2$ versus photon energy as it is shown in Fig. 10. We found that the E_g value for the films prepared in different deposition times varied from 3.78 eV to 4.03 eV, which is in agreement with what is reported by other authors [20]. The band-gap values are higher than the 3.7 eV measured in case of bulk zinc sulfide. This increase may be due to quantum confinement in the small crystals [21]. Also, the increase may be due to the presence of zinc hydroxide produced by the alkaline bath, thereby forming a mixture of zinc sulfur hydroxide $Zn(S,OH)$ [22].

It is clear from Fig. 10 that the gap energy values of the films before annealing are greater than those after annealing. The decrease in films band gap width after annealing could be attributed to improvement in the crystal structure and grain sizes change of the films after annealing. Table 2 shows the optical energy gap of ZnS thin films before and after annealing [23].

Fig. 10. The plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for ZnS thin films prepared in various deposition time.

Table 2. Gap energy values of ZnS thin films, before and after annealing.

Deposition time [min]	Direct band gap energy E_g [eV]	
	Before annealing	After annealing
60	4.03	—
90	3.91	3.83
120	3.87	—
150	3.96	—

The tail width E_{00} in the gap energy was obtained by plotting $\ln(\alpha)$ as a function of $h\nu$. The inverse of the slope extracted from the linear part gives E_{00} for the deposited ZnS films, as shown in Fig. 11. The E_{00} value increases with increasing the deposition time until it reaches the value of 120 min after which the tail width decreases. This result may be due to the fact that the increase in deposition time implies an increase in films thickness

(until $t = 120$ min) and this leads to an increase in film defects and localized states in the gap. As can be seen, the variation of optical gap is opposite to the disorder. This behavior indicates clearly that the optical gap is also controlled by disorder in the film.

Fig. 11. Optical gap and disorder variations of CBD-ZnS thin films as a function of deposition time.

Extinction coefficient (k)

The extinction coefficient (k) has been estimated from the following equation:

$$k = \alpha \lambda / 4\pi \quad (7)$$

where λ is the incident radiation wavelength.

Fig. 12 shows the evolution of the extinction coefficient as a function of wavelength for different deposition times of ZnS films. The extinction coefficient decreases as the wavelength increases and moreover it increases when the deposition time increases. This decrease in extinction coefficient may be the result of increased surface roughness as the film thickness increases, which induces an increase in surface optical scattering and extinction coefficient.

Fig. 12 shows also the extinction coefficient of the sample annealed at 500 °C for 120 min. From this figure, it can be inferred that the annealing process leads to the decrease of the extinction coefficient. This might be caused by the fact that the annealing process minimizes the defects or the tails depth (which means decreasing in the film absorbance).

Fig. 12. Extinction coefficient of nanocrystalline ZnS thin films, obtained in different deposition times versus wavelength, before and after annealing.

Fig. 13. Refractive index of nanocrystalline ZnS thin films versus wavelength in different deposition times, before and after annealing.

Refractive index (n)

The refractive index has been determined from transmittance spectra, as function of wavelength, using simple approximated relationship:

$$n = \frac{1+R}{1-R} + \left[\frac{4R}{(1-R)^2} - k^2 \right]^{1/2} \quad (8)$$

where R is the reflectance for an intermediate energy photon recorded by spectrophotometer, and k the extinction coefficient.

The refractive index variations in the wavelength range of 300 nm to 800 nm, for different deposition times, are shown in Fig. 13. It is seen that the refractive index increases when increasing the deposition time in the range spreading from 60 min to 150 min. This may be due to the film thickness increase and the formation of non-stoichiometric oxide phases in the ZnS films [24].

The figure also shows the effect of annealing process on the refractive index. It is clear that the annealing process induces a decrease in the refractive index values. After the annealing, the refractive index of the films is lowered by about 10 % in the visible range. This decrease is attributed to the fact that ZnS film surface begins to be oxidized when the film is annealed at 500 °C.

Moreover, Fourier transform infrared (FT-IR) studies were used to verify the presence of ZnS and other impurities existing on the surface of the films.

Fig. 14 shows the measured FT-IR spectra for the films of ZnS deposited at different deposition times on glass and monocrystalline silicon substrates. The absorption band located at 615 cm^{-1} can be attributed to the formation of ZnS phase [25]. The spectra show a large peak centered at 3360 cm^{-1} and a small peak at 1630 cm^{-1} , which are due to stretching and bending modes of H-OH. This might be due to trace amount of adsorbed water present on the film surface. The spectra show a small peak at 1110 cm^{-1} which is assigned to stretching mode of Zn-OH. The spectra also show a weak band in the region of 1475 cm^{-1} , which could be due to the bending modes of C-H. Based on this study, we can say that the film contains some amount of Zn(OH)_2 .

4. Conclusion

Economical chemical bath deposition (CBD) technique was used to deposit ZnS thin films with high transparency. Thin films of zinc sulfide were deposited onto glass substrate from the aqueous solution of zinc chloride, ammonia, thiourea and tri-sodium citrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7$) while Na_3 -citrate was used as the non-toxic complexing agent. The influence of deposition time was investigated in the present work. The thickness of ZnS films increased nearly linearly with time after

Fig. 14. Vertically shifted FT-IR spectra of a typical ZnS film deposited in different deposition times, (a) on glass (b) on monocrystalline Si substrate.

the nucleation phase (after 90 min). The X-ray diffraction analysis showed that the as-deposited films were amorphous. The annealing in air improved the film crystallinity with the formation of ZnO phase. The SEM images demonstrated a dense and uniform surface that was free of pits or pinholes. The well-defined spherical fine grains with different sizes were uniformly distributed over a smooth and homogeneous surface. The films exhibited also good adherence and covered the entire substrate surface. The EDX analysis confirmed the presence of zinc and sulfur in the ZnS thin films.

The optical properties of the films as-deposited and annealed at 500 °C for 120 min were also studied. The films were highly transparent. The percentage of transmission was around 82 % for all the as-deposited ZnS films in the visible range. For the annealed films, the percentages exceeding 82 % were achieved, except for the film deposited for 150 min, which showed only 70 % transmission of the film before annealing. The measured band gap was found to be in the range of 3.87 eV to 4.03 eV depending upon the deposition time.

References

- [1] FANG X.S., GAUTAM U.K., BANDO Y., DIERRE B., SEKIGUCHI T., GOLBERG D., *J. Phys. Chem. C*, 112 (2008), 4735.
- [2] HE J.H., ZHANG Y.Y., LIU J., MOORE D., BAO G., WANG Z.L., *J. Phys. Chem. C*, 111 (2007), 12152.
- [3] PRATAP S., PRASAD J., KUMAR R., MURARI K., *Defence Sci. J.*, 46 (1996), 215.
- [4] FANG X.S., BANDO Y., GAUTAM U.K., ZHAI T.Y., ZENG H.B., XU X.J., *Crit. Rev. Solid State*, 34 (2009), 190.
- [5] KURBATOV D., KSHNYAKINA S., OPANASYUK A., MELNIK V., NESPRAVA V., *Rom. J. Phys.*, 55 (2010), 213.
- [6] MURALI R.K., VASANTHA S., RAJAMMA K., *Mater. Lett.*, 2 (12 – 13) (2008), 1823.
- [7] WU X., LAI F., LIN L., LV J., ZHUANG B., YAN Q., HUANG Z., *Appl. Surf. Sci.*, 254 (2008), 6455.
- [8] ATEŞ A., YILDIRIM M.A., KUNDAKCI M., ASTAM A., *Mater. Sci. Semicond. Proc.*, 10 (2007), 281.
- [9] GHOSH P.K., JANA S., NANDY S., CHATTOPADHYAY K.K., *Mater. Res. Bull.*, 42 (2007), 505.
- [10] KRYSTAB T., KHOMCHENKO V.S., ANDRACA-ADAME J.A., ZAVYALOVA L.V., ROSCHINA N.N., RODIONOV V.E., KHACHATRYAN V.B., *Thin Solid Films*, 515 (2) (2006), 513.
- [11] BHALERAO B.A., LOKHANDE D.C., WAGH G.B., *IEEE. T. Nanotechnol.*, 12 (6), (2013), 996.
- [12] BALAMURUGAN D., JEYAPRAKASH B.G., CHANDIRAMOULI R., *J. Appl. Sci.*, 12 (2012), 1701.
- [13] HAUBI N.F., MIDHJIL K.A., RASHID H.G., MANSOUR H.L., *Mod. Phys. Let. B*, 24 (2010), 325.
- [14] GODE F., GUMUS C., ZOR M., *J. Cryst. Growth*, 299 (2007), 136.
- [15] CONTRERAS M.A., NAKADA T., HONGO M., PUDOV A.O., SITES J.R., *Proceedings 3rd World Conference of Photovoltaic Energy Conversion*, 2003, Osaka, 570.
- [16] KASSIM A., NAGALINGAM S., *Arab. J. Chem.*, 249 (2010), 234.
- [17] DUBROVIN I.V., BUDENNAYA L.D., MIZETSKAYA I.B., SHARKINA E.V., *Inorg. Mater.*, 19 (1983), 1603.
- [18] LIANG G., FAN P., CHEN C., LUO J., ZHAO J., ZHANG D., *J. Mater. Sci. Mater. El.*, (2015) 26, 2230.
- [19] ZHU H., HUANG J.F., WANG Y., CAO L.Y., HE H.Y., WU J.P., *Surface Eng.*, 27 (2013), 0267.

-
- [20] KANG S.R., SHIN S.W., CHOI D.S., MOHOLKAR A.V., MOON J.H., KIM J.H., *Curr. App. Phys.*, 10 (2010), S437.
- [21] GHOSH P.K., MITRA M.K., CHATTOPADHYAY K.K., *Nanotechnology*, 107 (2005), 16.
- [22] LOKHANDE C.D., PATIL P.S., TRIBUTSCH H., EN-NAOUI A., *Sol. Energ. Mat. Sol. C.*, 55 (1998), 379.
- [23] OFFIAH S.U., UGWOKE P.E., EKWEALOR A.B.C., EZUGWU S.C., OSUJI R.U., EZEMA F.I., *Digest J. Nano Mater. Bio Struct.*, 7 (1) (2012), 165.
- [24] ARENA O.L., NAIR M.T.S., NAIR, *Semicond. Sci. Technol.*, 12 (1997), 1323.
- [25] YANG H., ZHAO J., SONG L., *Mater. Lett.*, 57 (15) (2003), 2287.

Received 2017-12-13

Accepted 2019-04-23