Chalcogenide Letters Vol. 13, No. 5, May 2016, p. 217 - 224

CHARACTERIZATION OF AMORPHOUS CuS THIN FILMS OBTAINED FROM FAST TIME AND LOW TEMPERATURE OF DEPOSITION

A. CARRILLO CASTILLO[a*], R. C. AMBROSIO LÁZARO[b],
E. M. LIRA OJEDA[a], M. A. DE LA MOTA GONZÁLEZ[a, c],
M. A. QUEVEDO LÓPEZ[d], M. MORENO MORENO[e],
V. R. GONZALEZ DIAZ[b], J. F. GUERRERO CASTELLANOS[b]
[a] *Universidad Autónoma de Ciudad Juárez Chihuahua,* Ave. Del Charro 610, Cd. Juárez, Chihuahua, 32310, México
[b] *Benemérita Unuversidad Autónoma de Puebla, Ave. San Claudio y 18 Sur, CU, 72570, Puebla, Mexico*
[c] *CONACYT,Dirección Adjunta al Desarrollo Científico, Dirección de Cátedras, Insurgentes Sur 1582, Crédito Constructor, D.F, Benito Juárez, Ciudad de México, 03940, México*
[d] *Universidad de Sonora. Hermosillo, Sonora, 83000, México.*
[e] *Instituto Nacional de Astrofísica Óptica y Electrónica, Luis Enrique Erro1, Sta Ma. Tonanzintla, Puebla 72840, México.*

This work reports the successful deposition of copper sulphide (CuS) thin films by Chemical Bath Deposition on ITO substrates at 27 °C at short deposition times from 20 until 40 minutes using two complexing agents triethanolamine and ammonia. The studies on the properties of the CuS thin films include: X-ray diffraction that indicated the amorphous structure of the material. The XPS characterization demonstrated that Cu and S atoms are presented in the amorphous films. The optical band gap values were in the range from 2.22 to 2.32 eV. The influences of annealing process on the structural, optical and electrical properties also were studied. The surface roughness of annealed samples showed smother surface as compared to their as-deposited. The electrical conductivity changed five orders or magnitude from 10 $(\Omega\text{-cm})^{-1}$ as-deposited to $5.0x10^{6}$ $(\Omega\text{-cm})^{-1}$ for annealed samples at 150°C. The route presented in this work allows deposit CuS thin films for short deposition times at room temperature. The characteristics obtained in the these films make them suitable candidates for device applications that require low temperature of processing and also low cost, like flexible electronics.

(Received March 26, 2016; Accepted May 13, 2016)

Keywords: Copper sulphide, amorphous thin films, chemical bath deposition, semiconductors.

1. Introduction

Copper sulphide (CuS) as semiconductor material has been studied and received attention for their applications in optical and electronic devices such as solar cells, super capacitors, gas sensor, electrochemical sensors, cathode materials in lithium rechargeable batteries, thin film coating for windows filter [1-6] and also in photo-catalysts [7]. In addition, CuS thin films have been proposed on the development of low cost and non-toxic materials for solar energy conversion and storage [8-9], and the low material requirement and low temperature of deposition make it good candidate for another field of application like flexible electronics [10].

CuS thin films have been obtained using chemical and physical methods. The chemical methods are based on: solution-based process such as chemical bath deposition CBD [1, 6, 11], ionic layer adsorption and reaction –SILAR [12], hydrothermal [13], photochemical deposition

* Corresponding author: amanda.carrillo@uacj.mx

[14] and spray pyrolysis [15-16]. Physical methods have used techniques like co-evaporation, ALD and sputtering [17-19]. Among the several techniques of deposition, CBD is widely used for synthesis and deposition of CuS due to various advantages such as large deposition area, availability for different types of substrates, low cost since no requires vacuum equipment, and one of the most important advantages is its relatively low temperature of processing, which is compatible with flexible polymeric substrates. In CBD technique the inorganic semiconductors are deposited on substrates immersed in solutions containing metal ions and a source of chalcogenide ions. There are many studies in literature about synthesis and characterization of CuS thin films obtained by CBD, the most of these studies have been focused on the effect of factors such as pH [11], solution and substrate temperature [20, 21], annealing temperature [22], deposition time [23, 20], molar concentration [15, 20], among others. However, in the CBD technique used to obtain CuS thin films, one of the drawbacks is the deposition rate and annealing temperature around 400^{o}C; thus some works have reported deposition times in the range from 3 to 20 hours [24, 25]. Recently, an alternative solution like microwave assisted chemical bath deposition (MA-CBD) have proposed for deposition this material, which can enhanced the deposition efficiency and adherence of the material [26], and another routes using of copper sulphide, thioacetamide mixed together with ligand of acetic acid [27]; or copper nitrate, ethylene glycol (C2H6O2) and thioacetamide with different pH [11] have been used to increase the deposition time to be suitable the CBD growth of the CuS films. In CBD to prevent the precipitation of metal hydroxides, a complexing agent is added; it also reduces the concentration of free metal ions, which helps to prevent rapid bulk precipitation of the desired product [28]. For the case of CuS thin films, these are deposited by simply immersing the substrates in a dilute solution containing copper and sulphur reactive species. Typically the CuS are obtained by the reaction between a copper salt and thiourea in an alkaline solution. The slow release of Cu^{2+} ions is achieved by adding a complexing agent (ligand) to the Cu salt to form a determined copper complex species; upon dissociation, results in the release of small concentrations of Cu^{2+} ions. The S^{2-} ions are supplied by the decomposition of thiourea. Therefore, the objective of this work is to deposit CuS thin films by using two complexing agents as route that can be attractive due to its low cost, low temperature of processing (room temperature) and faster deposition times than are reported in literature and to study materials properties. Thus, the elemental composition, surface morphology and crystalline structure of the CuS films obtained in this work were characterized by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and X-ray diffraction (XRD) respectively. The optical band gap was determined by Tauc's method from transmittance measurements. The electrical conductivity was determined from current-voltage characteristic by semiconductor characterization system.

2. Experimental Details

The CuS films were deposited by CBD using ITO substrates with dimensions of 2.5 cm×2.5 cm. Prior to the deposition of the films, these substrates were cleaned using TCE, acetone and deionized water, and then dried with Nitrogen. The films were prepared for different deposition times (20, 25, 35 and 40 minutes) while keeping all other bath parameters at the same. The solution was prepared from copper nitrate ($Cu(NO_3)_2$), triethanolamine ($C_6H_{15}NO_3$), ammonia (NH_4OH) as complexing agents and thiourea ($SC(NH_2)_2$) as a source of sulphur ions, in a volumetric ratio of 5 ml (0.5M): 2.5 ml (1M): 2.5 ml (29%): 5 ml (1M) respectively. The total reaction volume was adjusted with water to 43 ml. Stirring and heating of the mixture were processed by a hot plate. After a few seconds the ITO substrates were immersed vertically in the solution bath. The temperature of the solution was kept at 27 °C +/- 1°C, and the pH was about 11. We proposed the reaction mechanism for the deposition of (CuS) thin films as follows: with the use of two complexing agents and two sources of hydroxyl ions at the same time is possible to increase the deposition rate, thus, when triethanolamine and ammonia are used at the same chemical bath, there are two routes.

1) when the complexing agent is ammonia (NH3), the chemical reaction is:

$$Cu(NH_3)_4^{2+} \longleftrightarrow 4NH_3 + Cu^{2+} \quad (1)$$

The ammonia has been reported as complexing agent in the deposition of chalcogenide films, this compound help to control the velocity of the reaction [30-32].
2) when triethanolamine (TEA) acts as the complexing agent the chemical reaction is:

$$[Cu(TEA)]^{2+} \longleftrightarrow 4NH_3 + Cu^{2+} \quad (2)$$

TEA also has been reported as complexing agent in the deposition of chalcogenide thin films deposited by chemical bath, this compound acts to control the release of metalic ions [33-34]
In the mechanisms 1 and 2 there are two sources of Cu complexed, which are produced quickly. The hydrolysis of thiourea provides S^{2-} ions:

$$CS(NH_2)_2 + OH^-(H_2N)_2 \longleftrightarrow (H_2N)_2CO + HS^- \quad (3)$$

$$HS^- + OH^- \longleftrightarrow S^{2-} + H_2O \quad (4)$$

Finally:

$$Cu^{2+} + S^{2-} \longleftrightarrow CuS \quad (5)$$

After CBD deposition, the CuS films were cleaned in an ultrasonic bath with methanol followed by distilled water rinse and dried with N_2. Investigations of some chalcogenides films deposited by CBD reported annealing effects on chemical, optical and microstructural properties. In these works is reported that is possible obtain uniform films with good quality when those are annealed compared to as deposited [30-31, 35-37].

In the present work the films were annealed at 150 °C for 20 minutes in forming gas atmosphere in order to study its effect on the microstructure and the electrical conductivity.

The crystalline structure of the CuS films was investigated in a Rigaku Ultima III X-ray diffractometer with CuKα (λ)= 1.54 Å, operated at 40kV and 44mA. The 2Θ scan rate was 0.5°/min. The roughness of the films was measured by an atomic force microscope (AFM, Veeco, Model 3100 Dimension V) in a non-contact mode. Optical properties were studied by measuring absorbance of the films on a PerkinElmer Lambda 24 spectrophotometer within 300-900 nm wavelength range. Chemical analysis was achieved by the X-ray photoelectron spectroscopy analysis using a Perkin Elmer Phi 5600 ESCA system with an Aluminium (Al) X-ray source at 1 × 10-10 Torr of pressure. Gold Au contacts were deposited by sputtering in or-der to determine the electrical characteristics; (I-V) measurements at room temperature were performed in a 4200 Keithley semiconductor characterization system.

3. Results and discussion

The X-ray diffraction was performed for the four samples (20, 25, 35, 40 min) as-deposited and annealed respectively. Figures1 (a) and (b) show the XRD patterns, where is observed that there is not defined peak for CuS films, therefore a no defined plane for as-deposited and annealed samples was found, even after annealing the structure of the films remains amorphous, it is attributed due that the material was obtained at a low temperature. Such results a history mentioned by others [10-11, 38-40]. In all cases, only well-defined diffraction peaks of ITO substrate are present. Changes in the peaks preferred orientations of the ITO substrate is due to the thermal annealing (Figure 1 (a) Vs and (b))[41-43].

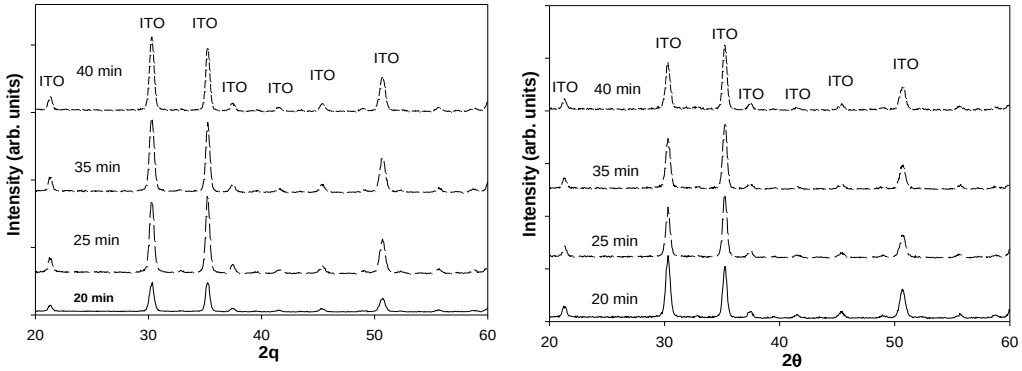


Fig. 1 XRD patterns of CuS films: a) As-deposited and b) Annealed at 150 °C for 20 minutes in forming gas.

XPS analysis was necessary to confirm the presence of Cu and S into the amorphous thin films. Optical characterization of CuS samples deposited over ITO substrates was performed using UV-Vis spectroscopy at room temperature. Figure 2 shows the transmittance spectra of CuS films obtained for different times of deposition. The transmission in the visible region is the range from 40 to 90 %, which is similar or higher than values reported in the literature [11, 17]. The transmittance of these films decreases with increasing of the deposition time, it is correlated with the increase in the film thickness as is shown in Figure 3. Additionally, another observation from Figure 2, is that in the near infrared region there is not a decreasing in the transmittance in contrast to report in the literature [6, 26, 29].

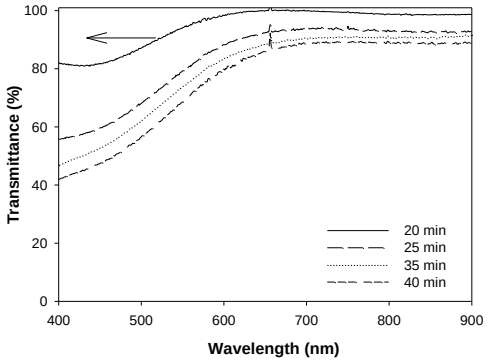


Fig. 2 Transmittance spectra of CuS films as deposited.

The absorption measurements were used to estimate the optical band gap. It was determined by the Tauc´s method. The optical band gap (E_g) for as deposited CuS films decreased from 2.32 to 2.22 eV as the thickness increased as is shown in Figure 4 and increase when the films were annealed. The decrease of the band gap in as deposited CuS films is attributed to improvement in the structure and change in grain size of the film [28] and the behavior of the band gap with increasing the film thickness has also been reported in references [12, 14]. And the increase in the band gap with annealing temperature has been reported as an improvement in the crystallinity in the films [31]. The range of band gap is in agreement with the values obtained for amorphous CuS thin films in [6,14, 24].

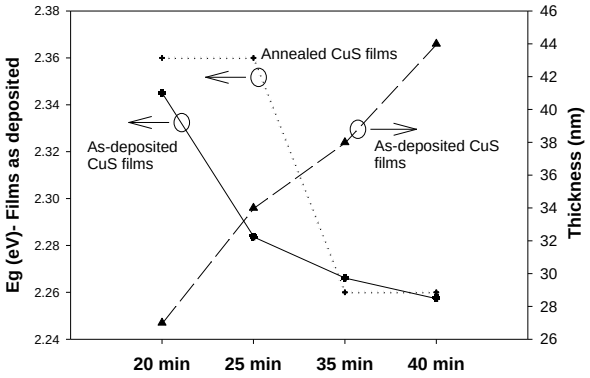


Fig. 3 Estimated band gaps of CuS films, and the thickness as a function of deposition time.

In Figure 3, is also shown the variation of film thickness as a function of deposition time. The thickness of CuS film increased with deposition time up to 40 min, it value correspond for the maximum thickness of the films equal to 44 nm. The deposition rate using the route presented in this work is higher in comparison with similar CBD method and room temperature [24, 27]. Atomic force microscope (AFM) was used to study the surface roughness of the CuS films deposited on ITO-substrates, for the analysis the films deposited at 25 and 35 min were selected. In Figure 4 is found that these thin films are uniform, without holes or cracks. Average thicknesses were obtained by measuring a film step with AFM and also by SEM cross section. Figure 3 and Figure 4 correlate that the surface roughness increased as the thickness of the thin films increases and decreased when the films were an annealed. The increasing in copper ions in the bath led to the formation of CuS particle too fast and promotes the growth of large particles in the films. In addition, the larger particles disappeared after annealing process, and exhibited a smoother surface as shown in Figure 4(d) compared to the as-deposited CuS.

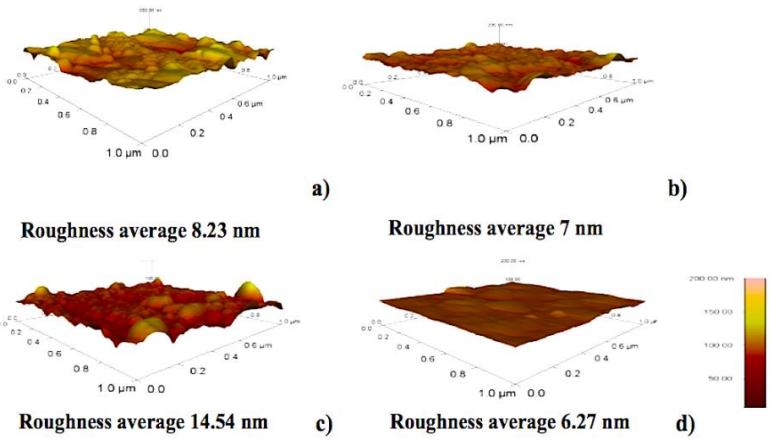
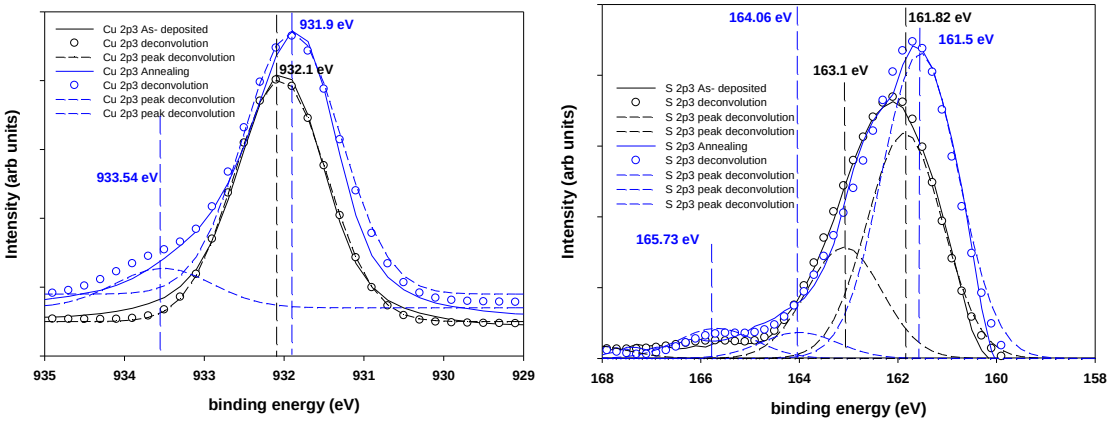


Fig. 4 AFM images of the samples: a) As-deposited b) with annealing process, both obtained at 25 min; c) As-deposited and d) with annealing process both obtained at 35 min.

The successfully synthesis and deposition of CuS thin films was demonstrated by the XPS measurements for as deposited and annealed CuS films. For this case, the sample deposited at 35 min. was analyzed. The Figure 5 (a) shows the XPS spectra, from it in the Cu 2p region the signal for Cu 2p3/2 is centered around 932.1 eV for the as-deposited CuS film. The CuS film annealed XPS spectra shows two peaks in the Cu 2p region at 931.9 and 933.54 eV. The structure at 932.1 and 931. 9 eV is concerned with Cu^{+}, whereas the structure at 933.54 eV can be described as Cu^{2+} [11, 22, 44-45] . In other words with annealing treatment on the films is possible to promote the

CuS phase formation. And also it is important to mention that others reported by the study of XPS the coexistence of Cu^{+} and Cu^{2+}.

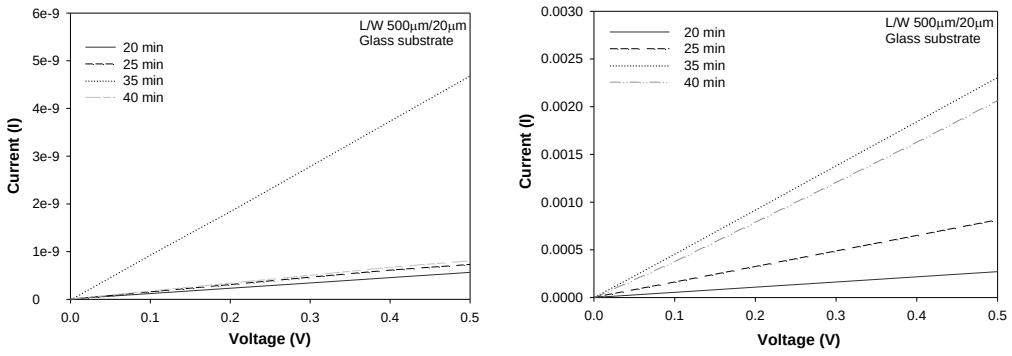
In the case of the S2p (Figure 5(b)) region it can be split into two apparent peaks for the as-deposited and annealed films. The first peaks located at a binding energy of 161.82 and 161.5 eV for as deposited and annealed sample respectively which correspond to CuS, and are in agreement with the CuS composition in [11, 22]. The second peak located at 163.1 and 164.06 eV for as deposited and annealed film corresponds to S-S peak position [45-47].



a) *b)*

Fig. 5 XPS spectra of a) Cu 2p3/2 and b) 2p1/2 in the CuS films deposited at 35 min.

The electrical conductivity of CuS films was determined from I-V measurements at 300 K in dark conditions under air atmosphere. In Figure 6 (a) and (b) are shown the current-voltage characteristics for as-deposited and annealed samples, it is seen that the metal-CuS interface has a good ohmic behavior. A remarkable larger forward current has been obtained for annealed CuS thin films, probably due to higher concentration of Cu or S ions as is demonstrate by XPS and an improvement of the surface, which result in an increasing on conductivity by five orders of magnitude, due to annealing could increase crystallinity of CuS. The resistance in CuS films decreases as a function of deposition time, due to dependence on the thickness. The resistivity for annealed films was on the range from $1.8x10^{-5}$ to $2.0x10^{-6}$ Ω-cm depending on deposition time. Therefore, the values of conductivity in this work are higher than reported for samples obtained by co-evaporation at 450°C [30], and for CuS annealed at 400°C deposited on polyimide foils [45]. In CBD technique the annealing processes is one of the main factor that affect the final properties of the films. In this study is demonstrated, because the surface roughness has influence on the electrical properties, which improves the conductivity after annealing due to reduction of the electron scattering effects [29-49].



a) b)

Fig. 6 Current-Voltage characteristics of CuS films a) As-deposited and b) Annealing

4. Conclusions

Chemical bath deposition process had been used to deposit CuS amorphous thin films on ITO substrates. The presented route using two complexing agents can easily deposit CuS films at short times and at room temperature. The adding of two sources of hydroxyl ions at the same time could increase the deposition rate on CBD compared for the standard process with one complexing agent. The average transmission in the visible region for the CuS films was on the range of 50-90 % depending of the time deposition. The optical band gap decreases as the thickness increased. The annealing process modified the surface and improved the electrical conductivity by five orders of magnitude. The XPS analysis confirmed the CuS compounds on the amorphous thin films. All of the deposited thin films showed a good ohmic behavior in the interface metal-semiconductor, with lower values of resistivity for annealed samples than reported in literature. These characteristics obtained for the amorphous CuS thin films make them a suitable candidate for device applications at low temperature processing.

Acknowledgements

The authors want express the thanks to UTD cleanroom staff. Also for SEP-CONACYT for their financial support Grants IOO17- 221117, in addition for PRODEP-SEP program for their support.

References

[1] P.K. Nair, M.T.S. Nair, J. Campos, L.E. Sansores, Sol. Cells **22**, 211 (1987).
[2] K.J. Huang, J.Z. Zhang, Y. Fan, J. Alloys Comp. **625**, 158 (2015).
[3] A. A. Sagade, R. Sharma, Sens. Actuators B **133**, 135 (2008).
[4] H.C. Tao, X.L. Yang, L.L. Zhang, S.B. Ni, J. Phys. Chem. Solids, **75**, 1205 (2014).
[5] A.K. Dutta, S. Das, P.K. Samanta, S. Roy, B. Adhikary, P. Biswas, Electrochim. Acta **144**, 282 (2014).
[6] M.T.S. Nair, P.K. Nair, Semicond. Sci. Technol. **4**, 191 (1989).
[7] D. Jiang, W. Hu, H. Wang, B. Shen, and Y. Deng, Chem. Eng. J. **189**, 443(2012).
[8] C. H. Lai, M. Yen Lu, L. J. H. Chen, J. Mater. Chem **22**, 19 (2012).
[9] C. H. Lai, K. W. Huang, J. H. Cheng, C. Y. Lee, B. J. Hwang and L. J. Chen, J. Mater. Chem. **20**, 6638 (2010).
[10] N. Pala, S.L. Rumyantsev, J. Sinius, S. Talapatra, M.S. Shur, R. Gaska, Electron. Lett. **40**, 273 (2004).
[11] E. Güneri and A. Kariper, J. Alloys Compd. **516**, 20(2012).
[12] S. Lindroos, A. Arnold, and M. Leskela, Appl. Surf. Sci. **158**, 75 (2000).
[13] X. Yu., X. An, Mater. Lett. **64**, 252(2010).
[14] J. Podder, R. Kobayashi, M. Ichimura, Thin Solid Films **472**, 71(2005).
[15] P. V. Nho, P. H. Ngan, N. Q. Tien, H. D. Viet, Chalcogenide Letters **9**, 397 (2012).
[16] C. Naşcu, I. Pop, V. Ionescu, E. Indrea, I. Bratu, Mater. Lett. **32**, 73(1997).
[17] A. Bollero, M. Grossberg, B. Asenjo, M.T. Gutierrez, Surf. Coat. Technol. **204** , 593 (2009).
[18] J. Johansson, J. Kostamo, M. Karppinen, L. Niinisto, J. Mater. Chem. **12**, 1022 (2002).
[19] H. Sánchez, A. Carrillo, J. Hernández, J. Faria, H. Camacho, P. García, C. Martínez, C. Rodríguez, ChalcogenideLetters **12**, 381 (2015).
[20] P. V.-Umnuay, C.-H Chang, ECS J. Solid State Sci. Techno **2** , P120 (2013).
[21] H. Y. He, Optoelec. and Advan. Materials, **5**, 1301 (2011).
[22] Y.-T. Nien, I.-G. Chen, J. Alloys Compd. **471** , 553 (2009).
[23] Y. Lu, X. Meng, G. Yi, J. Jia, J. Colloid Interface Sci. **356**, 726 (2011).
[24] N. Mukherjee , A. Sinha, G. G. Khan, D. Chandra , A. Bhaumik, A. Mondal, Mater. Res. Bull. **46**, 6 (2011).
[25] K.J.Wang, G.D. Li, J.X. Li, Q.Wang, J.S. Chen, Cryst. Growth Des. **7**, 2265 (2007).

[26] M. Xin, KW. Li, H. Wang, Appl. Surf. Sci. **256**, 1436 (2009).
[27] I. Puspitasari, T. Gujar , K. Jung, O. Joo, Mater Sci Eng B. **140**, 199 (2007).
[28] A. Carrillo, R. Ambrosio, E. Lira, C. Martínez, M. Quevedo, F. Aguirre, Chalcogenide Letters **10**, 421 (2013).
[29] A. Bollero, S. Fernández, K. Rozman, Z. Samardzija, M. Grossberg, Thin Solid Films **520**, 4184 (2012).
[30] Y. RodríguezLazcano, L. Guerrero, O. Gomez Daza, M.T. S. Nair, P.K Nair, Superficies y Vacio **9**,100(1999).
[31] S.M. Ho, Research Journal of Applied Sciences, Engineering and Technology **11(10),** 1058(2015).
[32] P.A. Ilenikhena, African Physical Review **2**, 0007 (2008).
[33] A. Carrillo Castillo, F.S. Aguirre Tostado, A. Salas Villasenor, I. Mejia, B.E. Gnade, M. Sotelo Lerma, M.A.Quevedo López, Chalcogeide Letters **10,** 105 (2013).
[34] I. Bencista, F. Di Benedetto, M. Innocenti, A. De Luca, G. Fornaciai, A. Lavacchi, G. Montegrossi, W. Oberhauser,L. A. Pardi, M. Romanelli, F. Vizza, M.L. Foresti, Eur. J. Mineral **24,** 879 (2012).
[35] A. Carrillo Castillo, A. Salas Villasenor, I. Mejia, S. Aguirre Tostado, B. E. Gnade, M.A. Quevedo Lopez, Thin Solid Films **520,** 3107(2102).
[36] O. L. Arenas, M.T.S, P.K. Nair, Semicond. Sci. Techol. **120,** 1323(1997)
[37] M. Ali, A. Ates, A. Astam, Physica **E41,** 1365(2009)
[38] A. Apolinar Iribe, M.C. Acosta Enriquez, D. Berman Mendoza, T. Mendivil Reynoso, E. Larios Rodrìguez, R.Ramirez Bon, S.J. Castillo, Chalcogenide Letters, **10,** 543 (2013).
[39] Ch. Usoh, Ch. Okujagu, I. Owate, Chemistry and Materials Research, **6 (5),** 1 (2014).
[40] M.A. Sangamesha, K, Pushapalatha, G. L. Shekar, International Journal of Research in Engineering and Technology,**2 (11),** 227(2013).
[41] M.Negiin, K. Alireza, A. Soleimani, Ebrahim, B, Sheida, Iran. J. Chem. Chem. Eng. **28 (2),** 57 (2009)
[42] D. . Raoufi, A. Kiasatpour, H. Reza Fallah, A. Sayd, Hassan, Applied Surface Science **253,** 9085 (2009).
[43] M. Gulen, G. Yildirim, S. Bal, A. Varilci, J. Mater Sci: Mater Electron **24 (2),** 467 (2012).
[44] Y.C. Zhang, T. Qjao, X. Ya, J. Cryst. Growth **268,** 64 (2004).
[45] J. Li, T. Jiu, G. H. Tao, G. Wang, Ch. Sun, P. Li, J. Fang, L. He, Journal of Colloid and interface Science **419**, 142(2014).
[46] Ch. D. Wagner, A.V. Naumkin, A. Kraut Vass, J. W. Allison, C.J. Powell, J.R. RumbleJr, NIST Standard ReferenceDatabase 20, Version 3.4.
[47] E. Kurmaev, J. Van Ek, D. Ederer, I. Zhou, T. Callcott, R. Perera, V. Cherkashenko, S. Shamin, V. Trofimova, S.Bartkowski. J. Phys: Condens. Matter. **10,** 1687 (1998).
[48] J. Cardoso, O. G. Daza, L. Ixtlilco, M. T. S. Nair, P. K. Nair, Semicond. Sci. Technol. **16**, 123 (2001).
[49] G. Palasantzas, Y.-P. Zhao, G.-C. Wang, T.-M. Lu, J. Barnas, J.Th.M. De Hosson, Phys. Rev. B **61**, 11109 (2000).