OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 8, No. 3-4, March – April 2014, p. 282 - 287

Fabrication of CdS thin films by chemical bath deposition

BAOYUN HU[a,*], ZHENZI JING[a], JIANFENG HUANG[b], FANGMING JIN[c]
[a]*School of Materials Science & Engineering, Tongji University, Shanghai 201804, China*
[b]*Key Laboratory of Auxiliary Chemistry & Technology for Light Chemical Industry, Ministry of Education, Shaanxi University of Science & Technology, Xi'an, 710021, China*
[c]*School of Environmental Science and Engineering, Shanghai Jiao Tong University, Shanghai, 200240, China*

Cadmium sulfide (CdS) thin films have been deposited on the ITO glass substrate using the chemical bath deposition (CBD) technique. The phase composition, surface morphology and optical property of the as-deposited films were investigated. The obtained CdS thin films were characterized by XRD, FE-SEM, EDS, XPS and AFM. Ultraviolet-visible (UV-Vis) spectroscopy was used to investigate the optical property. Results show that the deposited CdS nano-films are in high purity and quality, and the thin films exhibit a dense and crystalline surface morphology. The energy band gap of the CdS thin films is calculated to be 2.41eV. Good transmittance and excellent absorbency of the as-deposited thin films are observed.

(Received May 16, 2013; accepted March 13, 2014)

Keywords: CdS thin films, Chemical bath deposition, Optical property

---

1. Introduction

Cadmium sulfide (CdS), as typical semiconductor material of the II-VI group with a direct wide-band gap (2.42eV at room temperature), has excellent optical, electrical and photocatalytic properties [1-3]. The properties of CdS are attractive for many promising applications in ultraviolet light emitting diode, flat panel display, cathode ray tube, photoconductor, LED and optical windows for solar cells [4-8]. Therefore, enormous efforts have been devoted to the research of CdS films.

There are numerous preparation methods involving magnetic sputtering [9], electron beam evaporation [10], spray pyrolysis [11], pulsed laser deposition [12], chemical vapor deposition(CVD), sol-gel method, thermal evaporation [13-16], chemical bath deposition(CBD) [17-20] and self-assembly method [21-22] to prepare CdS thin films. There are some deficiencies because high vacuum conditions and expensive laboratory equipment are needed in the several methods of the above. However, it is known from the literature that there are many advantages to synthesis nanoparticles and thin films by deposition in aqueous solution [23-27]. It is simple, convenient, effective and can be easily applied to industrial scale crystallized thin films in solution [28-30]. Among these methods, the CBD and self-assembly method are both belong to liquid deposition method. In particular, the CBD technique is found to be the most suitable for the production of uniform, adherent and reproducible large area thin films [19]. Chemical bath deposition is already a widely applied strategy in synthesis and fabrication.

This work uses the CBD method to prepare CdS films, compared with other methods, CBD method is particularly important because of its simplicity, low cost and simple facility to obtain large area films [31]. And high vacuum conditions and expensive laboratory equipment are not needed using this method. Crystallization can be achieved at all scales using the CBD method. And a variety of thin films (such as In_2S_3 thin films, ZnO thin films, ZnS thin films and others) can be synthesized by CBD method [32-34].

In this paper, the CdS thin films were prepared by chemical bath deposition process. The CdS nanoparticles are synthesized in solution, and then the nanoparticles are deposited on pre-prepared ITO substrate surface to form ordered structure CdS films. The structure, morphology and optical properties of the prepared CdS thin films were systematically investigated.

2. Experimental procedures

2.1 Materials

All of the raw materials used in the experiment, includingCdCl$_2$·H$_2$O, CH_3CSNH_2, oleic acid and anhydrous ethanol were analytical grade without further purification. The solvent used in the experiment is distilled water. NH_4OH, HCl and H_2O_2 are used to clean the substrates.

2.2 Deposition of CdS thin films

The CdS thin films have been deposited by chemical bath deposition method using materials such as cadmium chloride ($CdCl_2·H_2O$) and thioacetamide (CH_3CSNH_2). The ITO glass (20× 20× 1 mm) was used as substrates. Before deposition, all ITO substrates were ultrasonically cleaned. First, the substrates were ultrasonically washed with solution A (H_2O : NH_4OH : H_2O_2=6 : 2 : 1) for 15 minutes to remove the acidic substance on the surface. Second, the substrates were ultrasonically cleaned in solution B (H_2O : HCl : H_2O_2 = 6 : 2 : 1) for 15minutes to remove the alkaline substance, and then the substrates were washed with deionized water and ethanol for three times, respectively.

The CdS films used for this research were fabricated by chemical bath deposition following the next sequence: In a typical synthesis process, 1.61g cadmium chloride ($CdCl_2·H_2O$) and 3.61g thioacetamide (CH_3CSNH_2) were weighed in accordance with the molar ration of Cd and S of 6. First, the 1.61g cadmium chloride were placed in a beaker, and then 2mL oleic acid were added drop wise on the $CdCl_2·H_2O$ to wrapped cadmium chloride particles. Second, added 100mL distilled water to the beaker and magnetically stirring for 15 minutes and then added 3.62 g CH_3CSNH_2 to the beaker, magnetic stirring for 20 minutes to form a uniform solution. The cleaned ITO glass substrate was fixed in the solution with a support, and then the beaker was sealed with cling films. After 6 hours, there were yellow thin films appearing in the surface of the ITO substrate.

After deposition, the CdS films were washed by deionized water and anhydrous ethanol to remove the loosely adhered CdS particles on the films. Subsequently, the collected CdS films were dried in vacuum drying oven at 80 °C for 30 minutes. The thin films were all smooth and well adhered which were difficult to be scraped off.

2.3 Characterization methods

The phase composition, morphology and optical properties of the as-synthesized films were characterized via X-ray powder diffraction (XRD), field-emission scanning electron microscope (FE-SEM), Energy Dispersive Spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and UV/Vis/NIR Spectrophotometer. The XRD pattern was investigated by a D/MAX-2200PC X-ray diffractometer with Cu Kα radiation (λ= 0.15406 nm) and a scanning rate of 8°/min (Rigaku, Japan). FE-SEM images were obtained on a JSM-7000F field-emission scanning electron microscope equipped with an energy-dispersive spectrometer (JEOL, Japan). X-ray photoelectron spectroscopy (XPS, Model MK-II) was employed to evaluate the composition and electronic structure of the as-prepared thin films using Al $K\alpha$X-ray with energy of 1486.6 eV. The surface morphologies of the as-prepared thin films were observed using an atomic force microscope (AFM, Model SPA400-SPI3800N). UV-vis spectra were collected on a Lambda 950 spectrophotometer (PerkinElmer, USA).

3. Results and discussion

3.1 XRD characterization of the CdS films

Fig. 1 shows the XRD pattern of CdS thin films prepared by chemical bath deposition at the molar ratio of $[Cd^{2+}]$ = 0.08 mol/L, S/Cd = 6. According to the standard JCPDS cards, all the diffraction peaks can be indexed as the hexagonal wurtzite structure CdS crystallites. It can be seen from Fig. 1 that the diffraction peaks at 2θ of 24.81°, 26.51°, 28.18° and 47.84° were indexed to (100), (002), (101) and (103) crystal face of hexagonal wurtzite structure CdS crystallites, and the *d* values and relative intensity are consistent with those of standard card (PDF No.41-1049) of CdS. It demonstrates that the as-deposited films were hexagonal crystal system in structure and the space group was P63mc (186). It is clearly shown that the diffraction peaks from the (002) plane of CdS are much higher than the others, which indicate the orientation growth of the films. In addition, no other phases were observed, suggesting the high purity of the as-deposited CdS thin films.

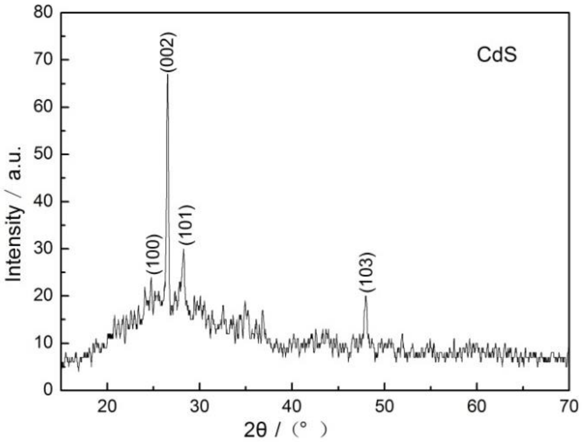

Fig. 1. XRD pattern of the CdS thin films prepared by chemical bath deposition($[Cd^{2+}]$ = 0.08 mol/L, S/Cd = 6).

3.2 FE-SEM characterization of CdS films

The surface morphology of the obtained CdS thin films were examined by FE-SEM and the images are shown in Fig. 2. As is shown in Fig. 2, three images show good surface morphology. Fig. 2(a) shows that the obtained CdS thin films are compose of many different sizes of polygons. Fig. 2(b) and Fig. 2(c), which are the high-magnification images of the CdS thin films of Fig. 2(a), show that the polygons with hierarchical structure are deposited by the smaller nanoparticles according to certain rules. It is observed that the crystalline grains of as-deposited CdS films are very small. The grain size is about 20 nm. Apparently, the nano-crystalline clusters coalesced to form large grains (the polygons) and there is apparent grain boundary between polygons. No pinholes were found in the films. From Fig. 2(c), it clearly can be seen that the surface morphology of the films were very smooth and uniform.

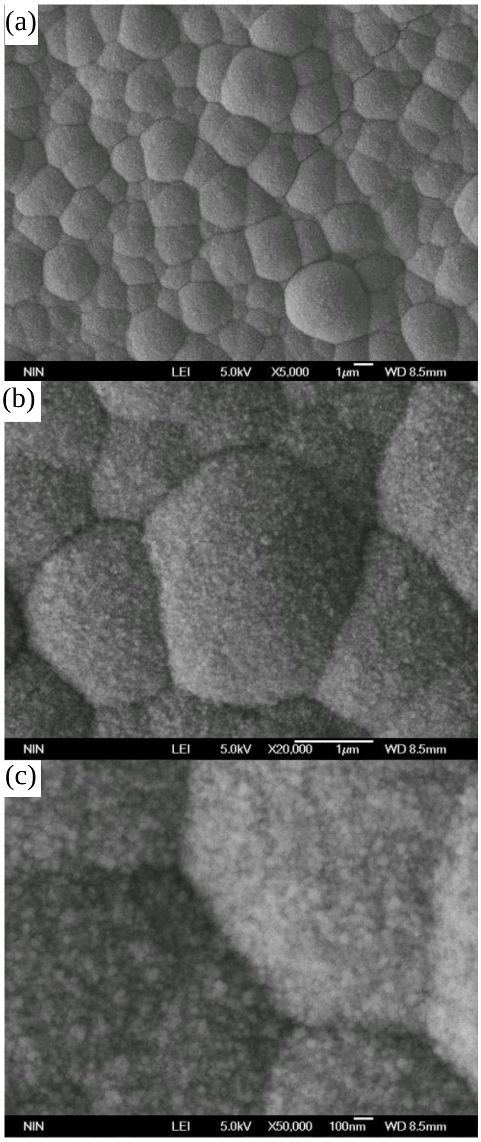

Fig. 2. FE-SEM images of the CdS thin films prepared by chemical bath deposition method.

3.3 EDS characterization of the CdS films

In order to further confirm the component of the CdS thin films, the as-deposited films were characterized by EDS, as shown in Fig. 3. The peak of cadmium Lα1 (3.13keV), Lβ1 (3.31keV), Lβ2 (3.53keV) and sulfur Kα1 (2.30keV) can be seen from Fig. 3. Cd and S are the primary composition elements and no other element is detected, which inferred that the as-prepared CdS films are in high purity. The atomic ratio of S and Cd is about 50.53:49.47 measured by the EDS analysis. This indicates that the ratio of sulfur and cadmium atom is very close to 1:1. Sulfur is a little excessive, and it may be associated with the excessive reactants of thioacetamide.

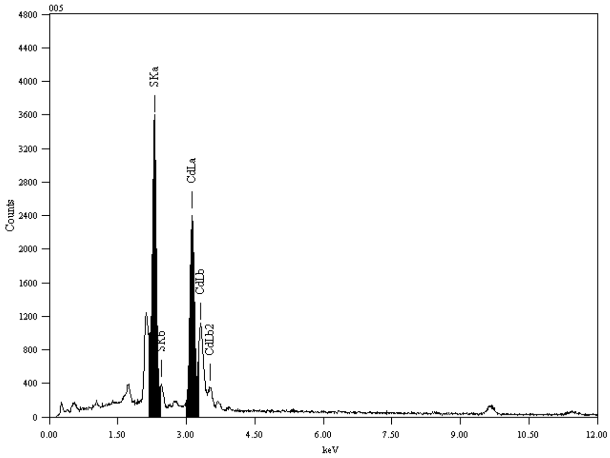

Fig. 3. Energy dispersion spectrum(EDS) of CdS thin films.

3.4 XPS characterization of the CdS films

The chemical composition of the as-deposited films was further characterized by XPS. The XPS spectrum in Fig. 4(a) shows there were no elements peaks observed other than Cd, S, C and O. The elements C and O came from the air and surface adsorption. No other peak was detected. This suggested that high purity CdS thin films had been obtained. Fig. 4(b) and 4(c) show the high-resolution spectra of the Cd and S regions, respectively. There are several Cd and S elements electron binding characteristic peaks from the lower binding energy to the higher, and the order is Cd3s, Cd3p, O1s, Cd3d, C1s, S2s, S2p, Cd4p, Cd4d spectral lines. XPS measurement usually needs C1s for calibration. The test results show that the binding energy of C1s is 282.9 eV, and C1s standard binding energy is 284.8 eV through the standard spectrum data, so the deviation of test result is $\Delta\delta$ = +1.9 eV [35-37]. Fig. 4(b) is the high-resolution spectrum of the peak around Cd3d in Fig. 4(a). The two peaks at 403.2 and 409.9 eV in Fig. 4(b) should be corrected to 405.1 and 411.8 eV because of the test result deviation $\Delta\delta$ = +1.9 eV. According to the standard spectrum data, the electron binding energy of Cd3*d*5/2 and Cd3*d*3/2 in CdS are 405.0 eV and 411.7 eV. It is clear that the two peaks corresponded to Cd3*d*5/2 and Cd3*d*3/2, respectively. This suggests that Cd element exists in the thin films mainly in the form of CdS. The electron binding energy in the vicinity of 773 eV is the electron peak Cd3s, however, it corresponded to the Cd in CdO. It is a mild oxidation in the surface of CdS films when placed in the air. Fig. 4(c) is the high-resolution spectrum of the peak around S2p in Fig. 4(a). It can be seen from the figure that the electronic strongest peak of surface S2p binding energy is at 160.20 eV, which suggests that element S combine with Cd, i.e. S exists in the thin films mainly in the form of CdS.

Table 1 is the quantization result of the peaks in Fig. 4(a). It shows that the peak binding energy of Cd3d, S2p, O1s and C1s is 403.25 eV, 160.20 eV, 530.40 eV and 282.90 eV, respectively. Considering of the deviation, the test results are consistent with the standard binding energy. The elements C and O are mainly from the pollution caused by the adsorption of large amounts of carbon and oxygen because the films were exposed in the air. Additionally, the atomic ratio of cadmium and sulfur in the CdS films is not strictly confined to 1:1, and the sulphur is slight excess, which indicates that the prepared CdS films are the rich sulphur type.

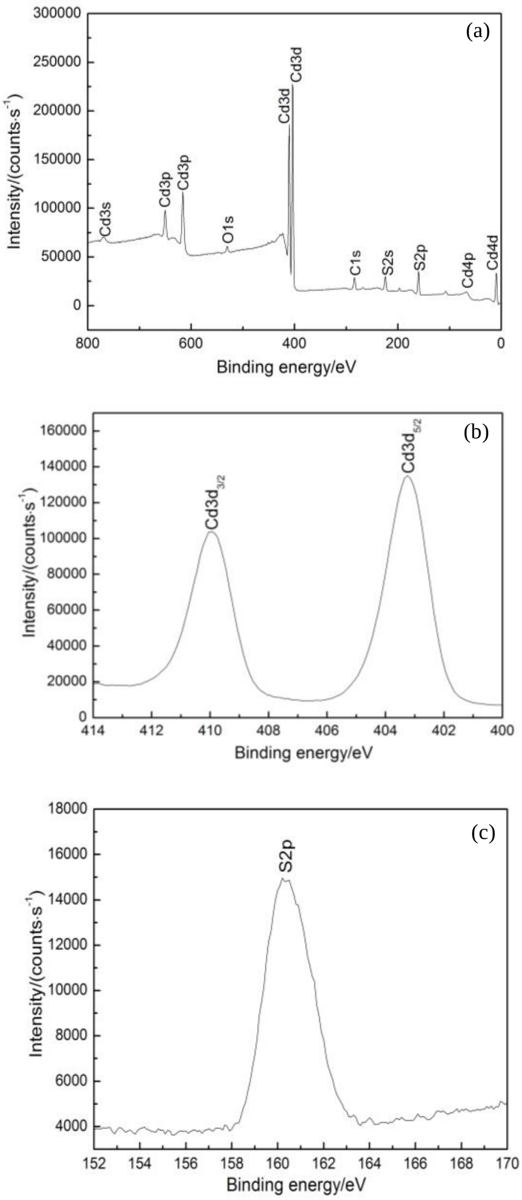

Fig. 4. X-ray photoelectron spectra of the CdS thin films (a : Survey scan; b : Cd region; c : S region).

Table 1. The atomic content on surface of the CdS thin films.

Peak	Bindingenergy (eV)	at.%
Cd3d	403.25	26.20
S2p	160.20	26.52
O1s	530.40	11.08
C1s	282.90	36.20

3.5 AFM characterization of the CdS thin films

Fig. 5 shows the AFM images of the as-deposited CdS thin films. According to the AFM images from Fig. 2, it can be seen that the prepared CdS thin films are uniform and dense, and the CdS thin films are composed of irregular polygons, which is consistent with the FE-SEM images results. The Fig. 5 also demonstrates that the up and downs of the surface is small and about several tens of nanometers, except a small number of large particles.

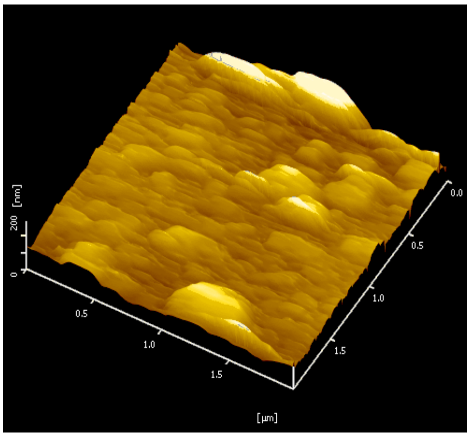

Fig. 5. AFM images of the CdS thin films prepared by chemical bath deposition.

3.6 Optical property analysis of CdS thin films

Fig. 6 shows the UV-visible transmittance spectrum of the CdS thin films prepared by chemical bath deposition method. The transmittance spectrum of CdS films was recorded from 200 to 800 nm. The spectrum indicates that the transmittance of the films is negative when the wavelength shorter than 400 nm, which reveals that the CdS films have a strong UV absorption capacity. When the wavelength greater than 500nm, the surface of the CdS films is becoming more and more smooth and the transmittance of the films will reach about 88%, indicating that the transmittance of the as-deposited CdS thin films is good.

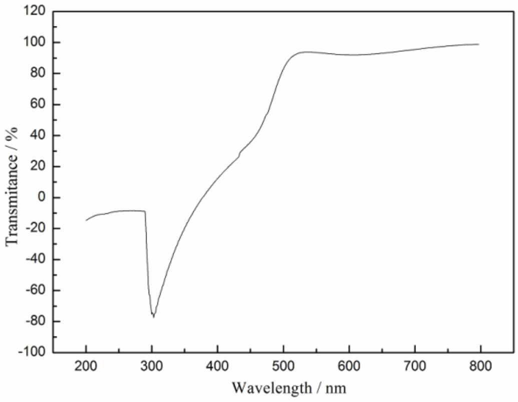

Fig. 6. UV-Vis transmittance spectrum of as-deposited CdS thin films.

Fig. 7 is the curve of the relationship between $(\alpha h\nu)^2$ and $h\nu$ of the CdS thin films. The absorption coefficient (α) was calculated from the transmittance spectrum (Fig. 6), using the equation $T = (1-R)^2 exp(-\alpha d)$ [38], where T is the transmittance, R the reflectance and d the films thickness. The band gap is related to the absorption coefficient by $(\alpha h\nu)^n = A (h\nu-Eg)$, where A is a constant, Eg is the optical band gap, $h\nu$ is the photon energy and n is taken 2 as for direct band gap materials or 1/2 for indirect band gap materials [39]. CdS is a direct band gap semiconductor materials according to the semiconductor theory, therefore, the band gap Eg can be calculated by the formula $(\alpha h\nu)^2 = A (h\nu-Eg)$. Band gap Eg of CdS thin films can be draw by fitting the relationship between absorption coefficient near absorption edge and photon energy, as shown in Fig. 7. It can be seen that the CdS as-deposited films have a band gap of 2.41eV, and the value agrees well with the 2.42 eV band gap of single crystalline CdS at room temperature [40], which shows the good stoichiometry of the as-deposited CdS films. The band gap of the as-deposited CdS films is a little red shift compare to that of CdS bulk materials (2.45 eV). It is well known that the semiconductor nanoparticle's energy gap decreases with increasing the grain size, which leads to a red shift of the optical absorption edge. The FE-SEM images in Fig. 2 show that the as-prepared CdS films are nanoscale thin films, but the nano-effect generally results in the blue shift of the absorption edge, so here the redshift may be due to the defect which existed within the films and an increase in sulfur deficiencies.

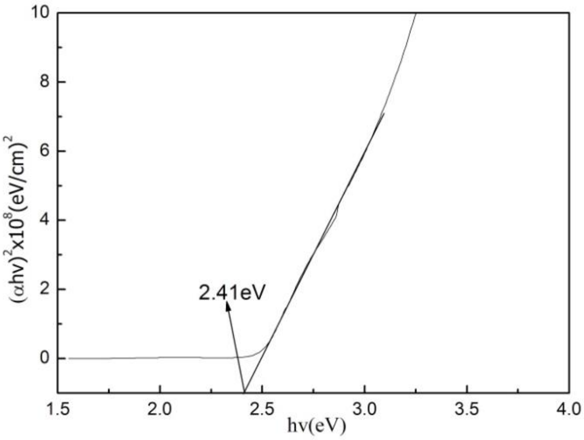

Fig. 7. Relationship between $(\alpha h\nu)^2$ and hv of the as-deposited CdS thin films.

4. Conclusions

From the experimental results presented in this paper in detail, the following conclusions about the as-deposited CdS thin films can be obtained: Smooth and uniform CdS thin films were successfully deposited at atmospheric environment by chemical bath deposition in this study. The XRD pattern revealed that the CdS thin films had a hexagonal phase with a preferential (0 0 2) orientation. EDS and XPS results showed that the prepared CdS thin films with high purity. FE-SEM and AFM micrographs indicated that the CdS thin films surface with good morphology, and the crystalline grains of as-deposited CdS films were very small (about 20nm). The UV-visible transmittance spectra derived that the as-deposited CdS thin films were translucent and the band gap was determined to be 2.41 eV, and a small amount of red shift may be attributed to the internal defects of the as-deposited CdS thin films.

Acknowledgements

This work reported here was financially supported by the National Natural Science Foundation of China (No. 51072138, 51272180).We thank Prof. Jian-peng Wu for technical assistance, and thank Shaanxi University of Science & Technology for providing XRD facility.

References

[1] H. Khallaf, I. O. Oladeji, L. Chow, Thin Solid Films **516**, 5967 (2008).
[2] X. F. Duan, Y. Huang, R. Agarwal, C. M. Lieber, Nature **421**, 241(2003).
[3] X. T. Sui, T. Zeng, G. C. Yin, H. Cheng, X. J. Zhao, Optoelectron. Adv. Mater.– Rapid Comm. **5**(3), 220 (2011).
[4] C. Burda, X. Chen, R. E. Narayanan, M. A. Sayed, Chem. Rev. **105**, 1025 (2005).
[5] Y. W. Jun, J. S. Choi, Cheon, J. Chem. Int. Ed. **45**, 3414 (2006).
[6] B. Y. Hu, J. F. Huang, L. Y. Cao, H. Zhang, J. P. Wu, Chinese J. Inorg. Chem. **26**(6), 1039 (2010).
[7] M. Savelli, J. Bougnot, Appl. Phys. **31**, 213(1979).
[8] B. Y. Hu, Z. Z. Jing, J. F. Huang, J. Yun, Trans. Nonferrous Met. Soc. China **22**, s89 (2012).
[9] S. Bonilla, E. A. Dalchiele, Thin Solid Films **204**, 397 (1991).
[10] K. Sivaramamoorthy, S. A.Bahadur, M. Kottaisamy, K. R. Murali, J. AlloysComp. **503**, 170 (2010).
[11] A. A. Yadav, E. U. Masumdar, J. Alloys Comp. **509**, 5394 (2011).
[12] B. Ullrich, H. Sakai, Y. Segawa, Thin Solid Films **385**, 220 (2001).
[13] X. Fu, L. Lin, D. B. Wang, Colloids Surf. A**262**, 216 (2005).
[14] H. Lee, H. Yang, P. H. Holloway, J. Phys. Chem. B **404**, 4364 (2009).
[15] H. Uda, H. Yonezawa, O. Yoshikazu,K. Manabu, S. Hajimu, Sol. Energy Mater. Sol. Cells **75**, 219 (2003).
[16] K. D. Rout, T. L. Haslett, L. Ryan, Chem. Phys. **210**, 343 (1996).
[17] J. Hernández-Borja, Y. V. Vorobiev, R. Ramírez-Bon, Sol. Energy Mater. Sol. Cells **95**, 1882 (2011).
[18] Y. V. Vorobiev, P. P. Horley, J. H. Borja, H. E. Esparza-Ponce, R. R. Bon, P. Vorobiev, C. Pérez,

J. G. Hernández, Nanoscale Res. Lett.**7**, 483 (2012).
[19] L. J. Kong, J. M. Li, G. L. Chen, C. F. Zhu, W. F. Liu, J. Alloys Compd. **573**, 112(2013).
[20] Z. Rizwan, B. Z. Azmi, M. G. M. Sabri, Optoelectron. Adv. Mater.– Rapid Comm. **5**(4), 393 (2011).
[21] Y. Chen, S. Zhou, X. Yang, J. Non-Cryst. Solids **356** (25), 1272 (2010).
[22] F. Huang, X. Lin, C. Cheng, P. Chen, Appl. Surf. Sci. **258**, 7359(2012).
[23] Y. F. Gao, K. Koumoto, Cryst Growth Des. **5**(5), 1983 (2005).
[24] F. Zhao, Y. F. Gao, H. J. Luo, Langmuir, **25**(12), 6940 (2009).
[25] F. Zhao, Y. F. Gao, H. J. Luo, Langmuir, **25**(23), 13295 (2009).
[26] Y. F. Gao, M. Nagai, J. Am. Ceram. Soc. **90**(3), 831 (2007).
[27] Y. F. Gao, M. Nagai, W. S. Seo, K. Koumoto, Langmuir **23**, 4712 (2007).
[28] Y. F. Gao, Masayuki Nagai, Langmuir, **22**, 3936 (2006).
[29] Y. Gao, M. Nagai, Y. Masuda, F. Sato, W. S. Seo, K. Koumoto, Langmuir, **22**, 3521 (2006).
[30] Y. F. Gao, H.J. Luo, Z. Zhang, L. T. Kang, Z. Chen, J. Du, M. Kanehira, C. Cao, Nano Energy, **1**(2), 221 (2012).
[31] C. Gao, H. Shen, L. Sun, Z. Shen, Mater. Lett. **65**, 1413(2011).
[32] S. B. Jambure, S. J. Patil, A. R. Deshpande, C. D. Lokhande, Mater. Res. Bull. **49**, 420(2014).
[33] B. Yahmadi, N. Kamoun, C. Guasch, R. Bennaceur, Mater. Chem. Phys. **127**, 239(2011).
[34] W. Liu, C. Yang, S. H. Hsieh, W. J. Chen, Chi-Lon Fern, Appl. Surf. Sci. **264**, 213 (2013).
[35] Y. F. Gao, Y. Masuda, T. Yonezawa, K. Koumoto, Chem. Mater. **14**, 5006(2002).
[36] L. T. Kang, Y. F. Gao, H. J. Luo, Z. Chen, J. Du, Z. Zhang, ACS Appl. Mater. Interf. **1**(10), 2211 (2009).
[37] G. Hotaa, S. B. Idageb, Kartic C. Khilar, Colloid Surf. A-Physicochem. Eng. Asp.**293**, 5(2007).
[38] F. deMoure-Flores, J. G. Quinons-Galvan, A. Hernandez-Hernandez, A. Guillen-Cervantes, M.A. Santana-Aranda, L. Olvera, M. Melendez-Lira, Appl. Surf. Sci. **258**, 2459 (2012).
[39] D. Dwyer, R. Sun, H. Efstathiadis, P. Haldar, Phys. Status Solidi A **207** (10), 2272 (2010).
[40] S. M. Sze, K. K. Ng, Physics of Semiconductor Devices, John Willey & Sons, New Jersey, 2007.

---

[*] Corresponding author: hubaoyun01@gmail.com