Journal of Alloys and Compounds 509 (2011) 5947–5951

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

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

The effect of substrate bias voltage on PbTe films deposited by magnetron sputtering

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ARTICLE INFO

Article history:
Received 1 December 2010
Received in revised form 3 March 2011
Accepted 3 March 2011
Available online 10 March 2011

Keywords:
PbTe films
Magnetron sputtering
Substrate bias

ABSTRACT

The PbTe films were deposited onto ITO glass substrate by radio frequency magnetron sputtering. Effect of external direct current electrical field applied between substrate and target on the quality of films was investigated. Stylus surface profile, X-ray diffraction (XRD), atomic force microscope (AFM) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the films. The film thickness was measured by a conventional stylus surface profile. The crystal structure and lattice parameters of films were determined by using XRD. The surface morphology of the films was measured by AFM. The absorption coefficients and optical band gaps of films were found from FTIR. The sheet resistance of the samples was measured with a four-point probe and the resistivity of the film was calculated. All the obtained films were highly textured with a strong (2 0 0) orientation. With increasing bias voltage to −30 V, the property of crystal structure, surface morphology and absorption coefficients and resistivity were improved. However, further increase of substrate bias leads to transformation of the property.

1. Introduction

Much attention has been paid to PbTe due to its potential application as a thermoelectric material, an infrared detector and a semiconductor laser in the 3–30 μm [1]. For its use in any of the above applications, PbTe films are desirable. Various techniques have been developed for the preparation of PbTe films, including chemical vapor deposition [2], electrodeposition [3], molecular beam epitaxy [4,14], atomic layer deposition [5], hot-wall epitaxy [6], vacuum evaporation [7], magnetron sputtering [8], wet chemical synthesis [11] and so on.

Among these various techniques, magnetron sputtering is the most common technique and is widely used in industry. The composition, microstructure and the properties of PbTe films deposited by magnetron sputtering vary with sputtering conditions, such as, substrate bias, nitrogen press and deposition temperature. Although much research has been carried out on the PbTe films deposited by magnetron sputtering [8–10], the information on the change of texture and properties with the applied substrate bias voltage is limited. In addition, Sn-doped In_2O_3 (indium tin oxide: ITO) films with thickness of 50 nm deposited on glass were chosen as substrate due to its high electrical conductivity and high transparency in visible regions. The characteristic of the multilayer would be discussed in another paper. In this paper, we investigated the microstructure and properties of PbTe films deposited on ITO films with different substrate bias voltages while keeping other parameters constant during the deposition process. And the phase structure, surface morphology absorption coefficients and resistivity of PbTe films were systematically studied.

2. Experimental process

The PbTe target (φ 60 mm × 5 mm) with 99.99% purity employed as source was purchased commercially (from Haite Materials). The target-to-substrate distance was 80 mm. Substrate of ITO films was progressively cleaned in an ultrasonic bath with acetone, methanol, isopropyl, alcohol and then rinsed in deionized water before the deposition process, in order to remove organic contaminants. Prior to deposition, the chamber was evacuated to a base pressure of 5.0×10^{-4} Pa, and the working pressure was 0.4 Pa in pure Ar. A radio frequency (RF) power source was used for sputtering and the input power was set at 30 W with zero reflected power. After the targets were sputtered clean for 15 min, PbTe films were sputtered for 10 min with a negative direct-current (dc) bias of 0, −20, −30, −40 and −50 V. And the deposited PbTe films are denoted as PbTe (V). For example, PbTe (−20 V) is a PbTe film reactively sputtered by −20 V substrate bias while keeping other parameters constant. No external heating or cooling of the substrate was used during deposition process.

The film thickness was measured by a conventional stylus surface profile (Tencor Alpha). In order to get accurate deposition rate, the PbTe films for 60 min with various bias voltages while keeping other parameters constant were deposited. So the thicknesses of the films are large enough to reckon the accurate deposition rate. The crystal structure of the deposited films was identified by XRD (Rigaku D/max) using Cu Kα radiation. The data was collected and calculated from Bragg's law [22]. The coating surface morphology and roughness were examined by AFM (Park Autoprode CP) in contact mode with UL06 tips. The absorption coefficients and optical band gaps of films were determined by using FTIR. The sheet resistance of the samples was measured with a four-point probe and the resistivity of the film was calculated.

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doi:10.1016/j.jallcom.2011.03.019

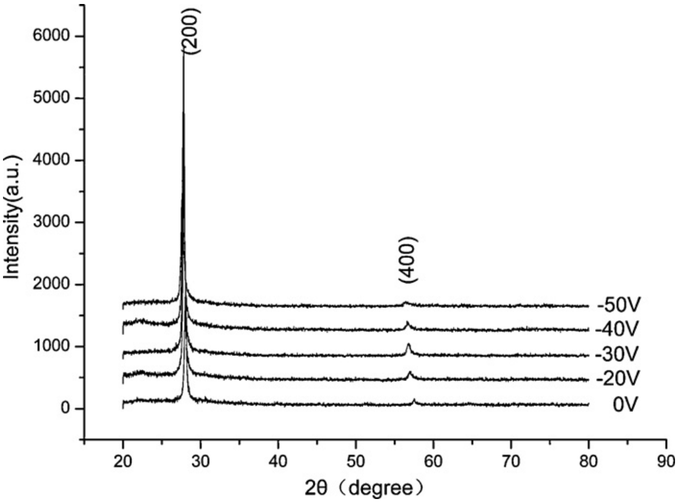

Fig. 1. XRD of PbTe films sputter deposited on ITO substrate at 30 W for 10 min with various bias voltages.

3. Results and discussion

Table 1 shows the deposition rate and thickness of PbTe films deposited on ITO substrate with various bias voltages while keeping other parameters constant. Results indicated that the deposition rate increases with the bias voltage until substrate bias up to −30 V, which is consistent with the effect of low substrate bias by S.R. Das. This is due to the increased bias voltage attracting the ions to bombard the surface to provide extra energy for the growing films, resulting in a higher deposition rate [12]. Further increase of the substrate bias, the deposition rate decreases. This is due to the high bias voltage make the clusters of the sputtered material more energy, which results in bombardment with surface more sharply. And the bombardment makes the number of molecules peeled off from the film [13].

Fig. 1 illustrates XRD profiles of the PbTe films deposited on ITO substrates with various biases and the XRD data is given in Table 2. The average grain size was calculated using the Sherrer equation

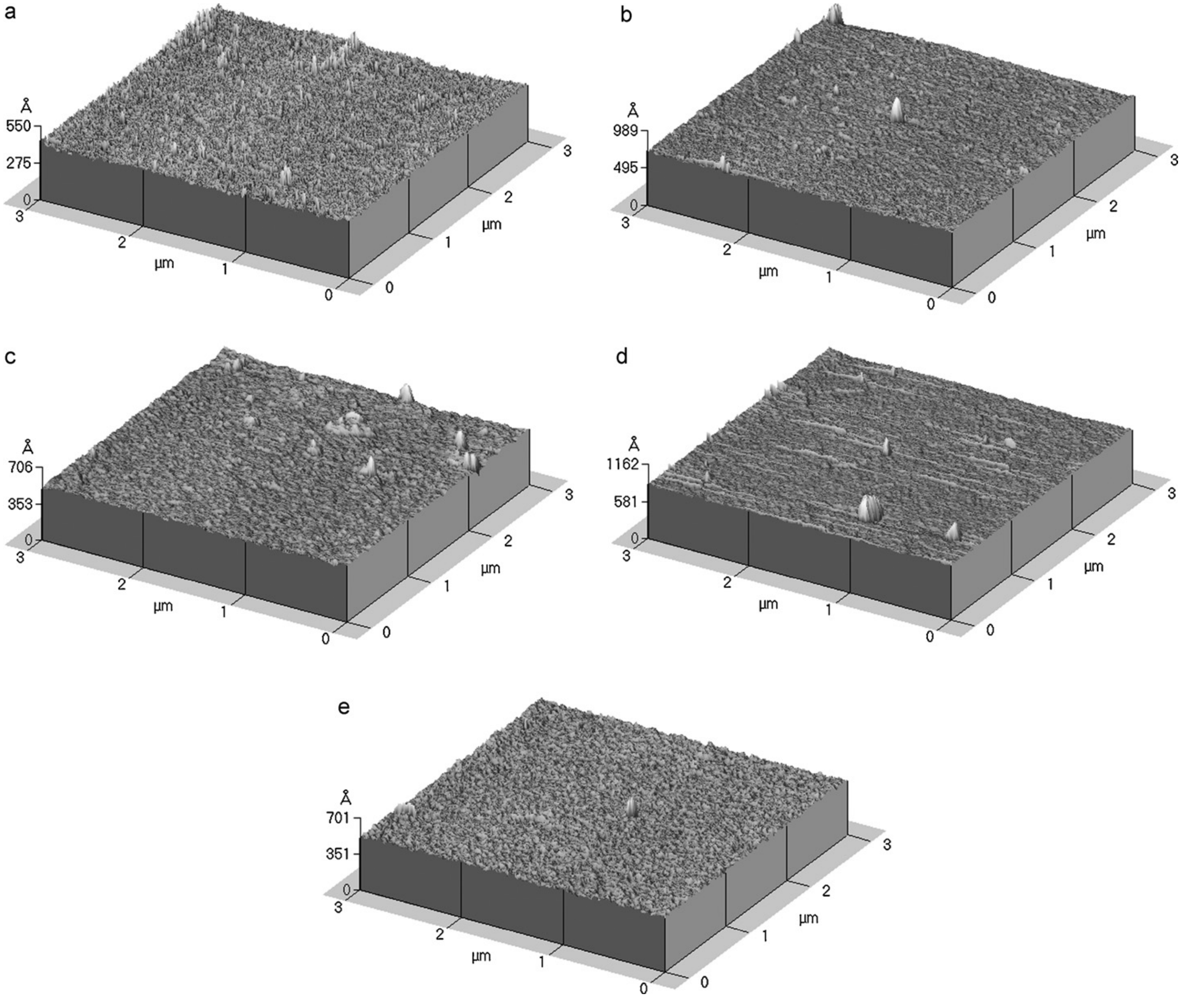

Fig. 2. AFM images of the three-dimensional configuration of the PbTe films deposited at 30 W for 10 min with various bias voltages: (a) sample PbTe (0 V); (b) sample PbTe (−20 V); (c) sample PbTe (−30 V); (d) sample PbTe (−40 V); (e) sample PbTe (−50 V).

Table 1
The deposition rate and thickness of PbTe films with various bias voltages.

	Substrate bias (V)				
	0	−20	−30	−40	−50
Thickness (nm)	184	233	278	237	235
Deposition rate (nm/s)	0.3072	0.3887	0.4639	0.3950	0.3918

Table 2
Structure parameters of PbTe films from (2 0 0) peak with various bias voltages.

Substrate bias (V)	2θ (°)	Intensity (a.u.)	FWHM (deg)	Grain size (Å)	*d* spacings (Å)	Lattice constant (Å)
0	27.982	1707	0.422	200	3.186	6.372
−20	27.840	3318	0.383	221	3.202	6.404
−30	27.819	4965	0.324	266	3.204	6.408
−40	27.741	3251	0.409	206	3.213	6.426
−50	27.620	1718	0.530	157	3.227	6.454

[25]:

$$\beta_{h,k,l} = \frac{0.9\lambda}{d\cos\theta} \quad (1)$$

where $\beta_{h,k,l}$ is the full width at half maximum (FWHM) of the (*h*,*k*,*l*) peak, *d* is the average grain size, λ is the incident wavelength (λ = 1.54178 Å), θ is the direction of propagation of scattered beams. Only the (2 0 0) peak and its second order peak can be seen in Fig. 1. All XRD patterns show sharp Bragg reflections, which indicate good crystallinity of samples. The patterns agree well with a cubic rock-salt type (that of PbTe). Further investigations on the reflections show a small but systematic shift to the low angle as the bias voltage increases. For example, as the bias voltage increases from 0 to −50 V, the shift of (2 0 0) can be easily observed from 27.982 to 27.620° in Table 2. This shift corresponds to a lattice expansion from 6.372 to 6.454 Å [2]. This is due to the increased bias voltage making the impinging particles deposited onto the substrate more energy. Because of the energy transferences between the impinging particles and the film surface, the more energy transfers to the crystal potential energy, which results in lattice expansion. In general, it has been reported that the grain size is reduced as bias is applied to substrate [15,16], however the grain size exhibit a different change in this work. As the substrate bias increases from 0 to −30 V, the average grain size increases from 200 to 266 Å. This is because the increased bias voltage make the impinging particles deposited onto the substrate more energy. And there would be more energy to transfer to the atoms and molecules of substrate surface, which accelerates grains growth [17]. As the bias voltage increases above −30 V, the average grain size decreases. This is due to the impinging particles with high energy making the number of molecules peeled off from the film, which blocks the grains growth. It seems that the best sputtering conditions according to Fig. 1 and Table 2 are deposited at 30 W for 10 min with −30 V substrate bias. This concept is based on the fact that under these conditions the highly textured film and the better grain size of PbTe could be obtained.

Three-dimensional surface morphologies of PbTe films deposited with various negative substrate bias voltages measured by AFM were illustrated in Fig. 2 and the root of mean square (RMS) roughness was plotted in Fig. 3. It is interesting to note that from sample PbTe (0 V) to sample PbTe (−30 V), the RMS roughness decreases from 15.5 to 10.8 Å. The change of surface roughness can be explained by the various substrate bias voltages. The increase of substrate bias voltage makes the atoms and molecules of the film surface more energy, which results in enhanced diffusion of atoms and molecules. So the PbTe films with lower roughness were prepared. However from sample PbTe (−30 V) to sample PbTe (−50 V), the surface roughness increases from 10.8 to 12.8 Å. Because when the sputtered species impinge onto the surface, there is not only energy transference between the sputtered species and film atoms, but also collision on the surface. Therefore, as the bias voltage increases above −30 V, the surface roughness consequently decreases. The results from AFM indicate that the surface roughness can be controlled by applying the bias voltage and lower roughness PbTe films can be attained with the bias voltage of −30 V.

The optical absorbance spectra of PbTe films with various bias voltages were measured at room temperature using a Fourier transform infrared spectrophotometer in the special range 3400–4100 nm at normal incidence. The absorption spectra of these films were studied to evaluate the absorption coefficient (α), forbidden energy gap (E_g). Absorption coefficient (α) = optical density/thickness [18–21]:

$$\alpha = \left(\frac{1}{t}\right) \log\left(\frac{I_0}{I_t}\right) \quad (2)$$

where *t* is the thickness of the PbTe films measured by a conventional stylus surface profiler, where I_0 is the incident intensity and I_t is the intensity after traversing.

The various types of transitions give rise to different frequency dependencies of the absorption coefficient near the fundamental

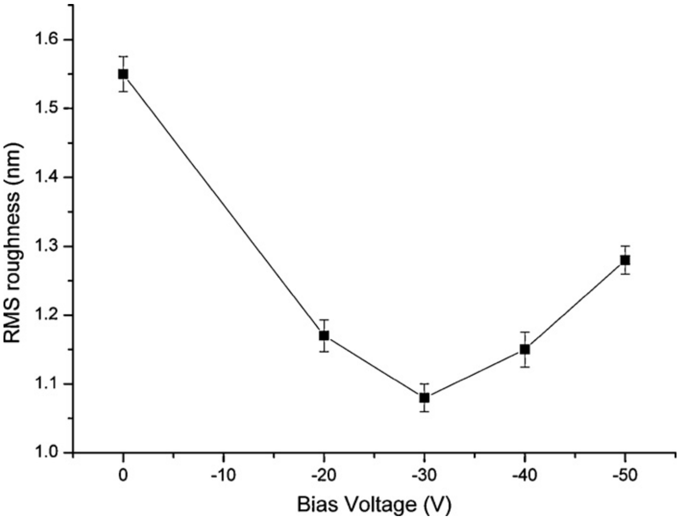

Fig. 3. Variation in surface RMS roughness of the PbTe films with substrate bias voltages.

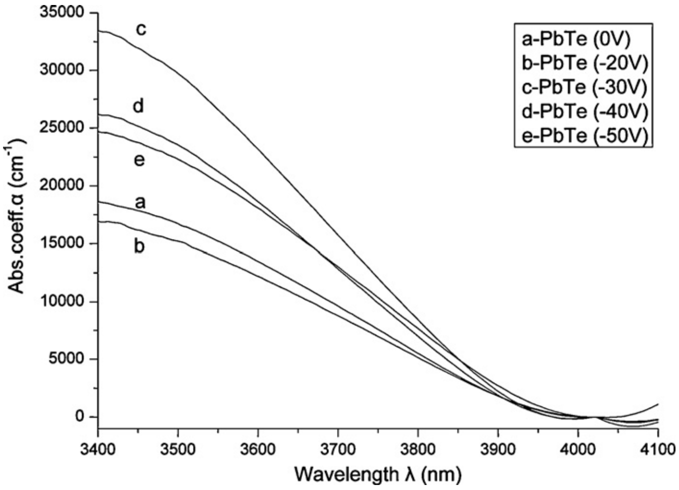

Fig. 4. Absorption coefficients (α) versus wavelength (λ) plots for PbTe with various bias voltages.

absorption edge [22–24]:

$$\alpha(h\upsilon) = A * (h\upsilon - E_g)^m \text{ cm}^{-1} \quad (3)$$

where the power factor $m = 0.5$ for allowed direct transitions, hυ and E_g being expressed in eV.

The variation of the absorption coefficient as a function of wavelength for PbTe films with various bias voltages is shown in Fig. 4. It is observed that the absorption coefficients for all these films are high ($\sim 10^4$ cm^{-1}) and increase sharply below the wavelength of 3900 nm. Especially the absorption coefficient of PbTe (−30 V) varies rapidly with wavelength. Fig. 5 presents the variation of $(\alpha h\upsilon)^2$ with $h\upsilon$ for PbTe films with various bias voltages. The intercepts (extrapolations) of these plots (straight lines) on the energy axis give the forbidden energy gaps [22]. It could be noted that the energy gaps range of the PbTe films with various bias voltages was from 0.324 to 0.327 eV and the lower value is associated with PbTe (−30 V). This may be due to highly texture with a strong (2 0 0) orientation and the better grain size of PbTe (−30 V).

Fig. 6 shows the dependence of bias voltage on the resistivity of PbTe films. As the bias voltage increases from 0 to −30 V, the resistivity decreases from 1.78 Ω cm to 1.00 Ω cm. When the bias voltage increases further, however, the resistivity increases. These variations are attributed to the variations of films thickness and the roughness affected by the bias voltage.

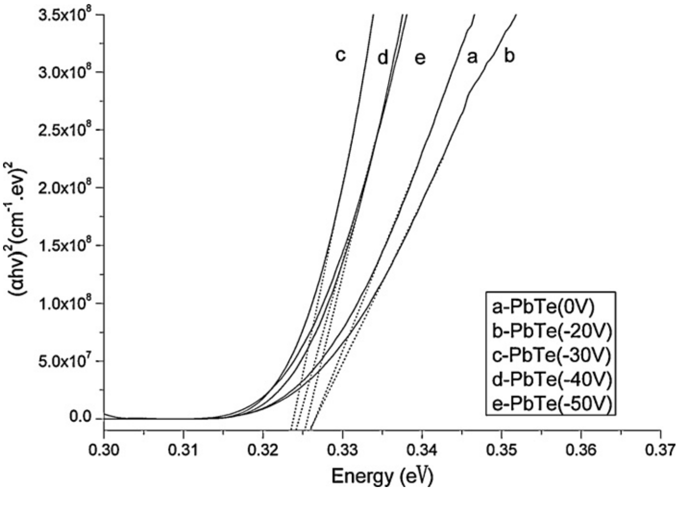

Fig. 5. $(\alpha h\upsilon)^2$ versus $h\upsilon$ plots for determination of band gaps of PbTe with various bias voltages.

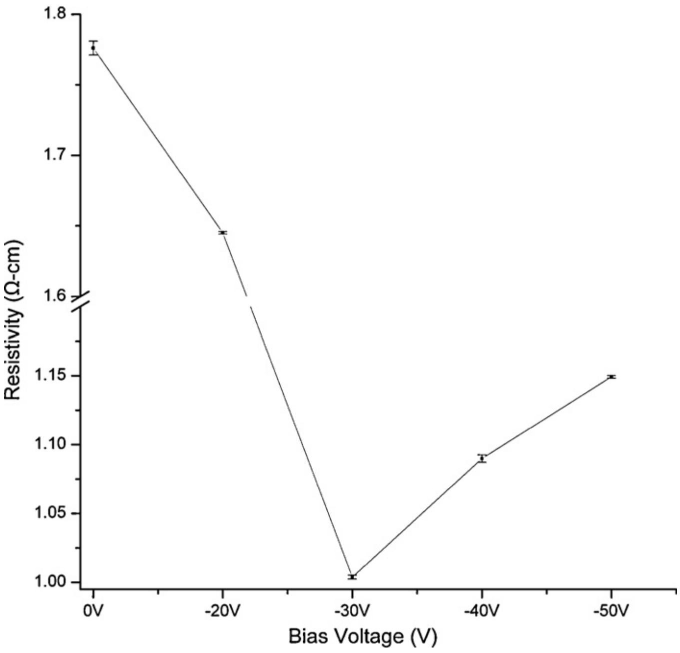

Fig. 6. Variation in resistivity of the PbTe films with substrate bias voltages.

4. Conclusions

In the present work, PbTe films were deposited on ITO substrate with various bias voltages by RF magnetron sputtering. It shows that the suitable bias voltage can improve the quality of the films by attracting the ions to bombard the surface to provide extra energy for the growing films. All the obtained films have a predominantly rock salt (NaCl) and were highly textured with a strong (2 0 0) orientation. The property of crystal structure, surface morphology, absorption coefficients, and resistivity were improved with the increasing of the bias voltage. However, if the applied bias is above −30 V, they will transform. With increasing the bias voltage, the lattice expanses, but the average grain size firstly increases and then decreases above −30 V. In addition, the surface morphology of films was obviously influenced by the bias voltage and the smoother PbTe film can be obtained with the bias voltage of −30 V. In all the obtained PbTe films, the absorption coefficient of PbTe (−30 V) films is very larger at $\sim 10^4$ cm^{-1}, the forbidden band gaps of direct type and the resistivity are lower. It indicates that the bias voltage of −30 V is the best condition for the preparation of PbTe films.

References

[1] A. Jdanov, Z. Dashevsky, J. Pelleg, R. Shneck, Mater. Res. Soc. Symp. Proc. 744 (2003) M5.29.1–M5.29.5.
[2] B. Zhang, J. He, T.M. Tritt, Appl. Phys. Lett. 88 (2006) 43119.
[3] F. Xiao, B. Yoo, M.A. Ryan, K.H. Lee, N.V. Myung, Electrochim. Acta 52 (2006) 1101.
[4] J.D. Koenig, M. Winkler, H. Boettner, J. Electron. Mater. 38 (2009) 1418–1422.
[5] D.O. Banga, R. Vaidyanathan, L. Xuehai, J.L. Stickney, S. Cox, U. Happeck, Electrochim. Acta 53 (2008) 6988–6994.
[6] A. Ishida, D. Cao, S. Morioka, M. Veis, Y. Inoue, T. Kita, Appl. Phys. Lett. 92 (2008) 182105.
[7] L. Kungumadevi, K. Rajasekar, A. Subbarayan, R. Sathyamoorthy, Ionics 14 (2008) 63–67.
[8] A. Jdanov, J. Pelleg, Z. Dashevsky, R. Shneck, Mater. Sci. Eng. B 106 (2004) 89–94.
[9] S.S. Sahay, S. Guruswamy, J. Mater. Sci. Lett. 17 (1998) 1145–1147.
[10] S.R. Das, J.G. Cook, M. Phipps, W.E. Boland, Thin Solid Films 181 (1989) 227–233.

[11] J.J. Urban, D.V. Talapin, E.V. Shevchenko, C.B. Murray, J. Am. Chem. Soc. 128 (2006) 3248–3255.

[12] H.L. Ma, X.T. Hao, J. Ma, Y.G. Yang, S.L. Huang, F. Chen, Q.P. Wang, H. Zhang, Surf. Coat. Technol. 161 (2002) 58.

[13] J.H. Lee, J.T. Song, Thin Solid Films 516 (2008) 1377–1381.

[14] H. Zogg, C. Maissen, J. Masek, T. Hoshino, S. Blunier, A.N. Tiwari, Semicond. Sci. Technol. 6 (1991) C36.

[15] M. Benegra, D.G. Lamas, M.E. Ferna’ndez, N. Mingolo, A.O. Kunrath, R.M. Souza, Thin Solid Films 494 (2006) 146.

[16] M. Flores, S. Muhl, L. Huerta, E. Andrade, Surf. Coat. Technol. 200 (2005) 1315.

[17] Y. Wang, C. Zhao, Z. Song, F. Cao, D. Yang, Appl. Surf. Sci. 253 (2007) 8858–8862.

[18] K.A. Rubin, M. Chen, Thin Solid Films 181 (1989) 129.

[19] Y. Maeda, H. Andoh, I. Ikuta, H. Minemura, Appl. Opt. 64 (1988) 1715.

[20] D.P. Gosain, T. Shimizu, M. Ohmura, M. Suzuki, T. Bando, S. Okano, J. Mater. Sci. 26 (1991) 3271.

[21] K. Oe, Y. Toyoshima, H. Nagai, J. Non-Cryst. Solids 20 (1976) 405.

[22] S. Kumar, Z.H. Khan, M.A.M. Khan, M. Husain, Curr. Appl. Phys. 5 (2005) 561–566.

[23] J.I. Pankove, Optical Processes in Semiconductors, Prentice-Hall, Englewood Cliffs, NJ, 1971.

[24] Y. Ravich, B.A. Effimova, I.A. Smirnov, Semiconducting Lead Chalcogenides, Plenum Press, New York/London, 1970.

[25] W.L. Bragg, The Crystalline State, vol. 1, 1946, p. 189.