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Preparation of delafossite-type $CuCrO_2$ films by sol–gel method

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ABSTRACT

High-quality *c*-axis oriented delafossite-type $CuCrO_2$ films were successfully prepared by a simple sol–gel method. The microstructure, optical properties as well as room temperature resistivity were studied. It was found that the grain sizes of $CuCrO_2$ films pretreated with different temperatures are different; the films were smooth and consisted of fine particles. The maximal transmittance of $CuCrO_2$ films can reach 70% in the visible region. Optical transmission data of $CuCrO_2$ films indicate a direct band gap and an indirect-gap of about 3.15 eV and 2.66 eV, respectively. The carrier mobility of the films pretreated at 300 °C is smaller than that of the films pretreated at a higher temperature, because of the stronger carrier scattering.

1. Introduction

Transparent conducting oxide (TCO) films with n-type conductivity are widely used as critical components in both light emitting devices such as light emitting diodes (LEDs) and light absorbing devices such as solar cells (also photodetectors) which are gaining considerable interest for their energy saving and energy production capability [1,2]. The current TCO industry is dominated by just few materials such as ZnO_{1-x}, ZnO:In/Al/F/B/Ga, $In_{1-x}Sn_xO_3$, SnO_2:F or Cd_2SnO_4, being exclusively n-type conductors [3,4]. Transparent p-type semiconductors have only recently come under intense investigation. The first report on p-type TCO films of NiO was published in 1993 [5]. Delafossites such as $CuScO_2$ [6], $CuFeO_2$ [7], $CuInO_2$ [8], $CuYO_2$ [9], $CuCoO_2$ [10] have been widely studied since the discovery of p-type conductivity in transparent $CuAlO_2$ thin films in 1997 [11], which initiated extensive interest in this type of materials. Even though the electrical performance of these materials will never be able to compete with the well-established n-type TCOs such as Al-doped zinc oxide (AZO) or indium-tin oxide (ITO) due to their intrinsic low carrier mobility. Among the delafossite structure oxides, the $CuCrO_2$ film has a conductivity of the order $1\,S\,cm^{-1}$, and upon doping with 5% Mg the conductivity can be improved to $220\,S\,cm^{-1}$, which is the largest conductivity in the ABO_2 systems [12]. Therefore, $CuCrO_2$-based materials [13–21] have attracted considerable scientific and technological attention, which can be considered as one of the candidates for applications.

Up to now, the preparation of delafossite structure films has mainly been carried out by pulsed laser deposition (PLD) [22–26] and sputtering [4,12]. Solution methods, such as sol–gel processing, were expected to be an alternative, competitive approach to prepare these conducting oxides. Thin films or fibers are produced directly from the solution by techniques such as dip-coating, spray-coating or spin-coating at a lower cost than those based on sophisticated vacuum systems. Recently, delafossite structure films such as $CuYO_2$ [27] $CuAlO_2$ [19,28], $CuFeO_2$ [29] have been successfully prepared via sol–gel method.

In recent articles [17,19], film preparation as well as physical and structural characteristic of $CuCrO_2$ film prepared via sol–gel technique were discussed. Nevertheless, their performance still had to be improved especially in the structural (non-oriented $CuCrO_2$ film) and optical properties (really low transmittance of 32% in the visible region). In this paper, we reported a simple sol–gel route to prepare high-quality *c*-axis oriented delafossite-type $CuCrO_2$ films with the transmittance of 70% in the visible region. The structural, optical and electrical properties of $CuCrO_2$ films are investigated.

2. Experimental details

Stoichiometric $Cu(CH_3COO)_2{\cdot}H_2O$ (99%) and $Cr(NO_3)_3{\cdot}9H_2O$ (99%) were dissolved in 10 mL propionic acid. The metallic ion (Cu^{2+} and Cr^{3+}) concentration was 0.2 M. The mixtures were stirred for several hours in order to get a transparent precursor solution. The precursor solution was spin-coated onto sapphire substrates at a rate of 5000 r/min, pretreated at 300–700 °C for 30 min in air. After repeating the above described procedure four times, all the films were finally sintered in a tube furnace at 900 °C for 1 h in flowing nitrogen gas (N_2).

X-ray diffraction (XRD) profiles were studied, using CuKα radiation ($\lambda = 1.5418$ Å), to observe crystallization process. The respective crystal sizes were calculated. Microstructures and film thickness were examined via scanning electron microscopy (SEM). Optical transmission spectra were investigated, and the band gaps of the $CuCrO_2$ thin films were calculated. The dc resistivity of the films was

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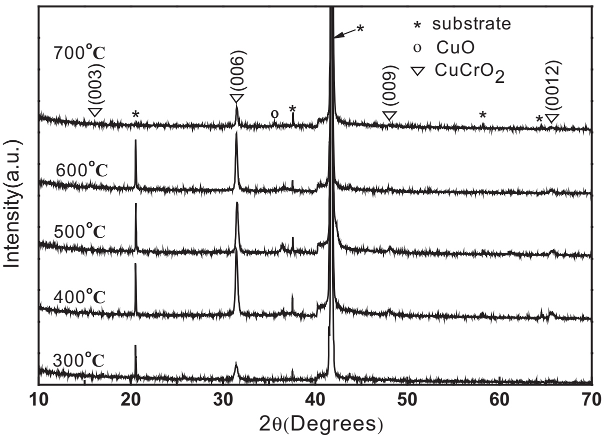

Fig. 1. XRD patterns of $CuCrO_2$ films pretreated at 300–700 °C, sintered at 900 °C for 1 h in flowing nitrogen gas (N_2). Peaks labelled as *, ○, and ▽ are attributed to the substrates, CuO, and $CuCrO_2$, respectively.

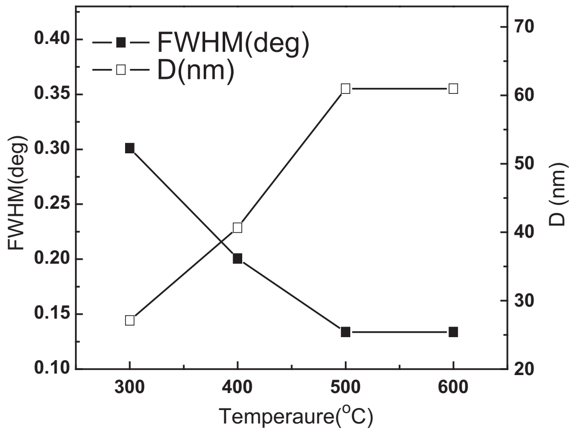

Fig. 2. Variations of the FWHM and the crystalline size as a function of the pretreating temperature obtained by analyzing the (0 0 6) signal at 31.4°. All samples have been sintered in nitrogen flow at 900 °C for 1 h.

measured by a Digital Multimeter and a two-probe configuration. Silver paste was used to create good ohmic contacts.

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the XRD results of the $CuCrO_2$ films pretreated at different temperatures (300–700 °C), sintered at 900 °C for 1 h in flowing nitrogen gas (N_2). From the XRD results, it can be found that the films pretreated at temperatures of 300–600 °C are composed of single delafossite-structured $CuCrO_2$ phase, as shown by ▽ in Fig. 1, without any detectable undesired phases. Moreover, it can be observed that the peak at 31.4° is especially sharp and have a significant lower line width than the other signals. This suggests that the film was well crystallized and highly *c*-axis oriented. Whereas the crystalline phase is difficult to confirm from the XRD pattern, it can be identified as either 3R or 2H. If it is considered to be the 3R phase, the four diffraction peaks shown in Fig. 1 are (0 0 3), (0 0 6), (0 0 9) and (0 0 12), respectively. The corresponding JCPDF Card No. is 89-6744. It can also be visualized as the 2H–$CuCrO_2$ phase, the four diffraction peaks are, instead, (0 0 2), (0 0 4), (0 0 6) and (0 0 8), respectively. The corresponding JCPDF Card No. is 89-6743.

However, when pretreated at 700 °C, an undesired weak diffraction peak about CuO phase is clearly observed as shown by ○ in Fig. 1. This fact reveals that the pretreating temperature of 700 °C is too high. From the Scherrer formula [30], the crystalline size can be calculated.

$$D_{hkl} = \frac{k\lambda}{\beta \cos\theta}$$

where k is a constant (~1), β is the full width at half maximum (FWHM), λ is the wavelength of X-ray and θ is the diffraction angle.

In Fig. 2 the FWHM and the crystallite sizes calculated by applying the Scherrer formula associated to the peaks at 31.4° and corresponding to the (0 0 6) plane of the delafossite are compared as a function of pretreating temperature. By increasing the pretreating temperature of $CuCrO_2$ films from 300 °C to 600 °C the crystallite size is increased from 27 nm to 61 nm. This fact suggests that higher pretreating temperatures provide higher energies for crystallizing the film.

Fig. 3 shows the SEM images of surfaces of $CuCrO_2$ films pretreated at temperatures of 400 °C and 600 °C, sintered at 900 °C for 1 h in flowing nitrogen gas (N_2). The surfaces of the films are smooth and consisted of fine particles. No cracks exist at the surface. It can be clearly seen that the particle size of sample (a) is smaller than that of sample (b), which is consistent with the results calculated from XRD patterns showed in Fig. 2. In order to estimate the thickness of the films, the cross-section FE-SEM is carried out. All films exhibited almost the same cross-sectional morphology regardless of the pretreated temperature. The thicknesses of $CuCrO_2$ films are 92, 88, 95 and 82 nm for $CuCrO_2$ films pretreated at temperatures of 300 °C, 400 °C, 500 °C and 600 °C, respectively. Fig. 4 shows the

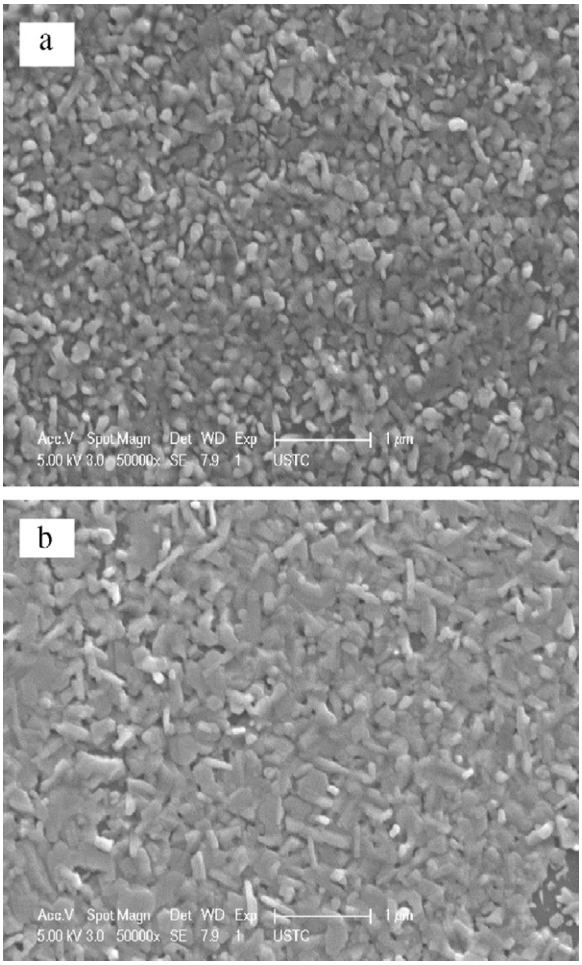

Fig. 3. SEM images of surfaces of $CuCrO_2$ films pretreated at temperatures of 400 °C (a) and 600 °C (b), sintered under nitrogen flow at 900 °C.

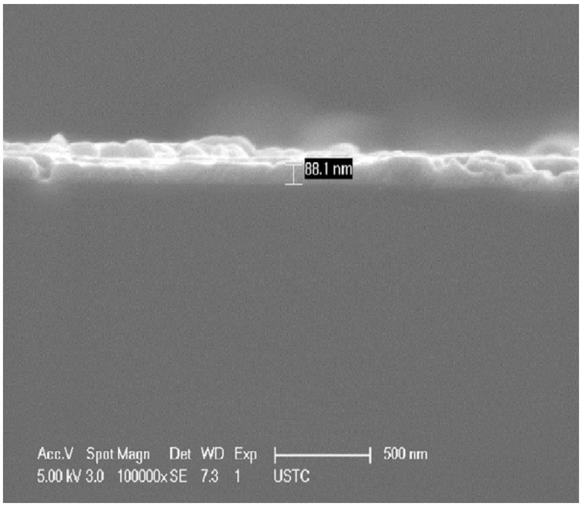

Fig. 4. Cross-section of $CuCrO_2$ film pretreated at 400 °C, sintered under nitrogen flow at 900 °C for 1 h.

typical SEM images of the cross-section of a $CuCrO_2$ thin film pretreated at 400 °C, sintered under nitrogen flow at 900 °C. The films are tightly attached to the substrates with thickness of about 88 nm.

3.2. Optical and electrical properties

The optical transmission spectra of $CuCrO_2$ films were investigated within the wavelength of 300–800 nm, and the results are shown in Fig. 5a. It can be seen that the visible light transmittances of $CuCrO_2$ films are decreased with pretreating temperature increasing. The average optical transmittances in the visible region are about 70%, 60% and 55% for the films pretreated at 300 °C, 400 °C and 600 °C, sintered under nitrogen flow at 900 °C for 1 h, respectively. Such high values for the films produced by the sol–gel method are much higher than previously reported 32% [17,19], and are comparable to those obtained by physical methods, such as PLD and RF sputtering. The lower transmittance of the films pretreated at a higher pretreating temperature may be due to increased photons scattering by pores in the films. The higher of the pretreating temperature, the easier and more pores are generated at the inner of the films. Scattering of photons attributed to pores in $CuCrO_2$ films of higher pretreating temperature would be stronger than that in lower pretreating temperature.

The absorption coefficients α can be calculated with the following formula:

$$I = I_0 e^{-\alpha l}$$

where I_0 is the incident intensity, I is the intensity of the transmitted light and l is the thickness of the films. The relationship of α and hv is shown in Fig. 5b. The value of absorption coefficients of $CuCrO_2$ films is rapidly increased when the photon energy is larger than 3 eV, and the optical absorption edge of $CuCrO_2$ films is formed. The fundamental absorption, which corresponds to electron excitation from the valance band to conduction band, can be used to determine the nature and value of the optical band gap of $CuCrO_2$ films. The relationship between the absorption coefficients α and incident photon energy hv can be written as:

$$(\alpha hv)^{1/n} = A(hv - E_g)$$

where A is a constant, E_g is the band gap of the material, hv is the photon energy, α is the absorption coefficient [31]. For a direct allowed transition, n is 1/2. For an indirect allowed transition, n is 2. $(ahv)^{1/n}$ versus hv is plotted with different n values and the results are shown in Fig. 6. From Fig. 6a, for the direct allowed transition, it can be obtained that the optical band gap are about 3.16 eV, 3.16 eV and 3.15 eV for the $CuCrO_2$ films pretreated at 300 °C, 400 °C and 600 °C, sintered under nitrogen flow at 900 °C for 1 h, from the portion of the plot to the hv-axis. This value is slightly larger than the theoretical calculation (2.55 eV) [32], but is quite constant with the value of literature reported [22]. As shown in Fig. 6b, for the indirect allowed transition, it can be obtained that the indirect-gap in $CuCrO_2$ films are about 2.7 eV, 2.66 eV and 2.62 eV, also is not very consistent with the theoretical calculation (2.04 eV) [32].

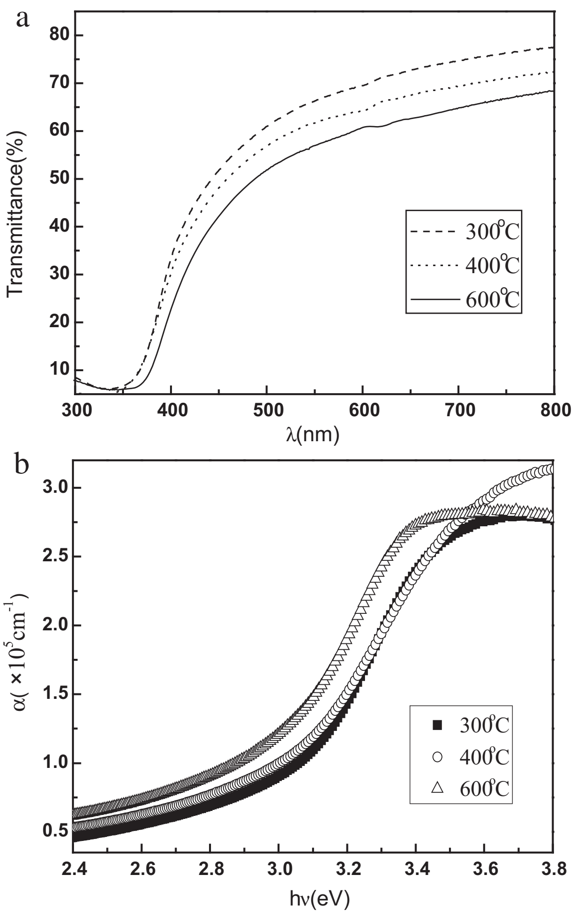

Fig. 5. Optical transmission spectra (a) and absorption coefficient (b) of $CuCrO_2$ films with different pretreating temperature. All samples have been sintered under nitrogen flow at 900 °C for 1 h.

In Fig. 7, the electrical properties of $CuCrO_2$ films are showed as a function of pretreating temperature. The room temperature resistivity of the film decreases along with pretreating temperature increasing from 300 to 400 °C, and then little changed. In our experiments, the change in resistivity is mainly due to three possible reasons, the change of the carrier concentration, the contact resistance and the carrier mobility. It is known to all, defect chemistry plays an important role in the p-type conductivity of transparent thin films. Presence of excess oxygen atoms within the crystallites sites or interstitial sites is responsible for the enhanced hole-conductivity [33]. However, in our experiments, all samples have been sintered at the same temperature of 900 °C under nitrogen flow for 1 h to initiate crystallization, to improve microstructure, to remove interstitial oxygen atoms and increase film density. Thus, the change of the carrier concentration caused by the unsaturated bonds as well as interstitial oxygen atoms is relatively small. Furthermore, silver paste was used to create good ohmic contacts in our experiments, so the influence of the contact resistance is tiny. On the other hand, it is widely accepted that in the lower

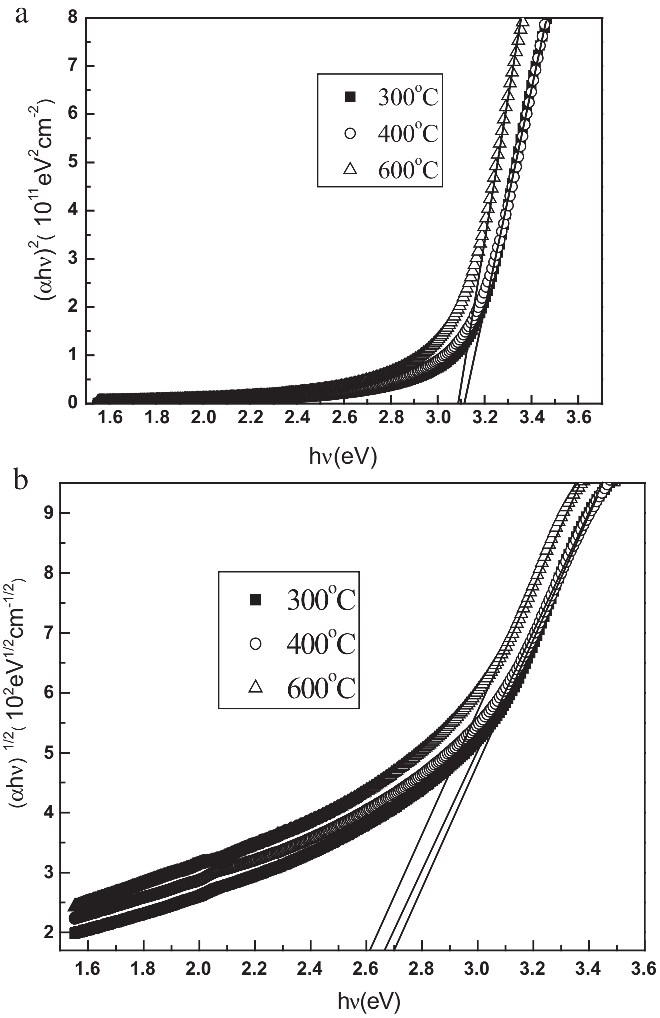

Fig. 6. Plots to test for direct allowed transition (a) and indirect band gap (b) for $CuCrO_2$ films.

crystallization system large amounts of defects such as grain boundaries will be introduced, which will increase the carrier scattering resulting in the increase of resistivity. Therefore, in our results, it is reasonable to suggest that the carrier mobility of the films pretreated at 300 °C is smaller than that of the films pretreated at a higher temperature, because of the stronger carrier scattering.

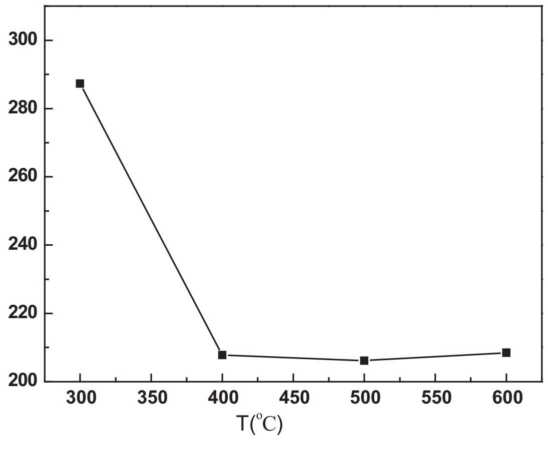

Fig. 7. Room temperature resistivity of $CuCrO_2$ films as a function of pretreating temperature. All samples have been sintered under nitrogen flow at 900 °C for 1 h.

4. Conclusions

In summary, the preparation of $CuCrO_2$ thin films on Al_2O_3 (0 0 *l*) substrates was carried out via the sol–gel method. The XRD results show that $CuCrO_2$ films are delafossite structure and high-quality *c*-axis oriented. The microstructure, optical properties as well as room temperature resistivity were studied. It was found that the films were smooth and consisted of fine particles. The SEM results reveal that the films are tightly attached to the substrates with thickness of 88.1 nm. The maximal transmittance of $CuCrO_2$ films can reach 70% in the visible region. Such high value for the films produced by the sol–gel method is comparable to those obtained by physical methods, such as PLD and RF sputtering. Optical transmission data of $CuCrO_2$ films indicate a direct band gap and an indirect-gap of about 3.15 eV and 2.66 eV, respectively. The carrier mobility of the films pretreated at 300 °C is smaller than that of the films pretreated at a higher temperature, because of the stronger carrier scattering.

The above results indicate the successful preparation of delafossite structure and high-quality *c*-axis oriented $CuCrO_2$ films with the transmittance of as high as 70% via sol–gel method. In the following research highly oriented $CuCrO_2$ films with high transmittance and conductivity prepared by sol–gel method still need to be developed.

Acknowledgments

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References

[1] D. Ginley, B. Roy, A. Ode, C. Warmsingh, Y. Yoshida, P. Parilla, C. Teplin, T. Kaydanova, A. Miedaner, C. Curtis, A. Martinson, T. Coutts, D. Readey, H. Hosono, J. Perkins, Thin Solid Films 445 (2003) 193.
[2] H.Y. Liu, V. Avrutin, N. Izyumskaya, U. Ozgur, H. Morkoc, Superlattices Microstruct. 48 (2010) 458.
[3] A.N. Banerjee, S. Kundoo, K.K. Chattopadhyay, Thin Solid Films 440 (2003) 5.
[4] A.N. Banerjee, K.K. Chattopadhyay, Prog. Cryst. Growth Ch 50 (2005) 52.
[5] H. Sato, T. Minami, S. Takata, T. Yamada, Thin Solid Films 236 (1993) 27.
[6] D. Shin, J.S. Foord, D.J. Payne, T. Arnold, D.J. Aston, R.G. Egdell, K.G. Godinho, D.O. Scanlon, B.J. Morgan, G.W. Watson, E. Mugnier, C. Yaicle, A. Rougier, L. Colakerol, P.A. Glans, L.F.J. Piper, K.E. Smith, Phys. Rev. B 80 (2009) 233105.
[7] M. Lalanne, A. Barnabe, F. Mathieu, P.H. Tailhades, Inorg. Chem. 48 (2009) 6065.
[8] K. Park, K.Y. Ko, H.C. Kwon, S. Nahm, J. Alloys Compd. 437 (2007) 1.
[9] N. Tsuboi, H. Ohara, T. Hoshino, S. Kobayashi, K. Kato, F. Kaneko, Jpn. J. Appl. Phys. 44 (2005) 765.
[10] M. Beekman, J. Salvador, X. Shi, G.S. Nolas, J. Yang, J. Alloys Compd. 489 (2010) 336.
[11] H. Kawazoe, M. Yasukawa, H. Hyodo, M. Kurita, H. Yanagi, H. Hosono, Nature 389 (1997) 939.
[12] R. Nagarajan, A.D. Draeseke, A.W. Sleight, J. Tate, J. Appl. Phys. 89 (2001) 8022.
[13] K. Singh, B. Kundys, M. Poienar, C. Simon, J. Phys.: Condes. Matter 22 (2010) 445901.
[14] Z.H. Deng, X.D. Fang, D. Li, S. Zhou, R.H. Tao, W.W. Dong, T. Wang, G. Meng, X.B. Zhu, J. Alloys Compd. 484 (2009) 619.
[15] J. Shu, X.D. Zhu,.T.F. Yi, Electrochim. Acta 54 (2009) 2795.
[16] S. Zhou, X.D. Fang, Z.H. Deng, D. Li, W.W. Dong, R.H. Tao, G. Meng, T. Wang, Sens. Actuators B: Chem. 143 (2009) 119.
[17] S. Gotzendorfer, R. Bywalez, P. Lobmann, J. Sol–Gel Sci. Technol. 52 (2009) 113.
[18] G.B. Dong, M. Zhang, X.P. Zhao, H. Yan, C.Y. Tian, Y.G. Ren, Appl. Surf. Sci. 256 (2010) 4121.
[19] S. Gotzendorfer, C. Polenzky, S. Ulrich, P. Lobmann, Thin Solid Films 518 (2009) 1153.
[20] W. Ketir, A. Bouguelia, M. Trari, Water Air Soil Pollut. 199 (2009) 115.
[21] P.W. Sadika, M. Ivilla, V. Craciuna, D.P. Norton, Thin Solid Films 517 (2008) 3211.
[22] D. Li, X.D. Fang, Z.H. Deng, S. Zhou, R.H. Tao, W.W. Dong, T. Wang, Y.P. Zhao, G. Meng, X.B. Zhu, J. Phys. D: Appl. Phys. 40 (2007) 4910.
[23] M. Neumann-Spallart, S.P. Pai, R. Pinto, Thin Solid Films 515 (2007) 8641.

[24] M.V. Lalic, J. Mestnik-Filho, J. Phys.: Condens. Matter 18 (2006) 1619.

[25] D. Li, X.D. Fang, Z.H. Deng, W.W. Dong, R.H. Tao, S. Zhou, J.M. Wang, T. Wang, Y.P. Zhao, X.B. Zhu, J. Alloys Compd. 486 (2009) 462.

[26] D. Li, X.D. Fang, A.W. Zhao, Z.H. Deng, W.W. Dong, R.H. Tao, Vacuum 84 (2010) 851.

[27] N. Tsuboi, K. Tosaka, S. Kobayashi, K. Kato, F. Kaneko, Jpn. J. Appl. Phys. 47 (2008) 588.

[28] J. Ding, Y.M. Sui, W.Y. Fu, H.B. Yang, S.K. Liu, Y. Zeng, W.Y. Zhao, P. Sun, J. Guo, H. Chen, M.H. Li, Appl. Surf. Sci. 256 (2010) 6441.

[29] S. Bassaid, M. Chaib, S. Omeiri, A. Bouguelia, M. Trari, J. Photochem. Photobiol. A: Chem. 201 (2009) 62.

[30] M.M. Bagheri-Mohagheghi, M. Shokooh-Saremi, Semicond. Sci. Technol. 19 (2004) 764.

[31] J.I. Pankove, Optical Processes in Semiconductors, Princeton University Press, New Jersey, 1971.

[32] D.O. Scanlon, A. Walsh, B.J. Morgan, G.W. Watson, Phys. Rev. B 79 (2009) 035101.

[33] A.N. Banerjee, C.K. Ghosh, K.K. Chattopadhyay, Sol. Energy Mater. Sol. Cells 89 (2005) 75.