Turkish Journal of Physics

http://journals.tubitak.gov.tr/physics/

Research Article

Turk J Phys
(2014) 38: 111 – 117
© TÜBİTAK
doi:10.3906/fiz-1301-17

XRD, XPS, and optical characterizations of Al-doped ZnO film grown on GaAs substrate

Ebru ŞENADIM TÜZEMEN[1,*], **Hülya ŞAHİN**[1], **Kamuran KARA**[2],
Sezai ELAGÖZ[1], **Ramazan ESEN**[2]
[1]Nanotechnology Center, Department of Physics, Cumhuriyet University, Sivas, Turkey
[2]Department of Physics, Çukurova University, Adana, Turkey

Received: 28.01.2013 • **Accepted:** 27.06.2013 • **Published Online:** 17.01.2014 • **Printed:** 14.02.2014

Abstract: A ZnO:Al (10%) thin film was prepared on GaAs(100) substrate by using a pulsed filtered cathodic vacuum arc deposition (PFCVAD) system. The ZnO:Al thin film was thermally annealed for 1 h at 2 different temperatures in air. The film structure was investigated as a function of annealing temperature by X-ray diffraction (XRD). ZnO:Al film annealed at 500 °C by PFCVAD method resulted in an amorphous film. However, after annealing ZnO:Al film at 600 °C, it showed (100) and (002) peaks at around 32° and 34°, respectively. The chemical state of ZnO:Al (AZO) film on GaAs substrate was investigated by using X-ray photoelectron spectroscopy (XPS). The dependence of optical properties on annealing was investigated by using a UV-VIS-NIR spectrophotometer. We also obtained the energy gap of ZnO:Al thin film by diffused reflectance spectra using the Kubelka–Munk function.

Key words: Al-doped zinc oxide, annealing temperature, diffuse and specular reflectance, optical band gap

1. Introduction

A zinc oxide (ZnO) film with a hexagonal wurtzite crystal structure is typically an n-type semiconductor. Because of its wide and direct band gap of 3.37 eV at 300 K and high transmission properties in the visible range with an exciton binding energy up to 60 meV, it is one of the promising candidates for fabricating ultraviolet (UV) light emitting diode and laser diode devices [1–5]. Transparent conductive oxide (TCO) thin films have been studied during the last decades for their luminescence and electrical properties. TCO thin films have been used generally for transparent conductive electrodes in photovoltaic applications and in display devices [6–8]. Among TCO films, Al-doped ZnO (AZO) films are being considered for manufacturing transparent electrodes due to their important properties, such as low cost, nontoxic nature, good electrical conductivity, good adhesion to substrate, chemical inertness, high luminous transmittance, and long-term environmental stability [9–12]. Many techniques for the preparation of ZnO films have been used; these include the sol-gel dip-coating technique [13], radio-frequency magnetron sputtering [14,15], direct current reactive magnetron sputtering [16], pulsed laser deposition [17,18], reactive chemical pulverization spray pyrolysis [19], sol-gel-derived technique [20], pulsed filtered cathodic arc technique (PFCVAD) [21], and chemical bath deposition [22]. The PFCVAD technique provides good adhesion and a dense, smooth, and better crystalline structure. ZnO thin films that are deposited using this technique have low resistivity and high optical transmittance in the visible region [23–27]. For these reasons, ZnO thin films that are deposited using the PFCVAD technique are ideal for the production of metal oxides and nitrides [28].

---

[*] Correspondence: esenadim@cumhuriyet.edu.tr

In this paper, the X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and optical properties of ZnO:Al (AZO) thin film prepared by PFCVAD technique are investigated.

2. Experimental

ZnO:Al thin film was grown on GaAs(100) substrate by PFCVAD using a metallic target (Zn/Al, 90/10; 1 mm in diameter), which was held in an alumina ceramic tube employed as a cathode target. The details of the deposition system were published in earlier study [29]. In this work, the substrate was kept at room temperature during the growth process. The base pressure of the deposition chamber was around 10^{-6} Torr and the working pressure was $\sim 7.6 \times 10^{-4}$ Torr. High purity (99.999% pure) oxygen was introduced into the chamber and controlled by a multi-gas controller. During deposition, the oxygen gas flow was fixed to 8 standard cm^3/min. While the film was being deposited, trigger voltage and arc voltage were set to 20 kV and 500 V, respectively. After deposition, the film was oxidized at 500 °C and 600 °C for 1 h in air.

We structurally characterized the ZnO:Al thin film grown on GaAs substrate by out-plane θ-2θ scans using a Rigaku SmartLab 9 kW rotating Cu anode system with 4-bounce monochromator.

XPS measurements were obtained with an X-ray photoemission spectrometer using Al Kα (hν = 1486.6 eV) radiation from an X-ray source operated at 10 kV with a current setting of 20 mA for detailed spectra and 5 mA for overview spectra. Photoelectrons were detected with a hemispherical analyzer. The spectrometer pass energy settings were 20 eV for the detailed spectra and 50 eV for the overview spectra.

Diffuse reflectance of the ZnO:Al film was measured over a wavelength range of 200–800 nm, using a double-beam UV-VIS-NIR spectrophotometer (Cary 5000, Varian) with a Cary 5000 Internal Diffuse Reflectance Accessory consisting of a integrating sphere of 110 mm in diameter. Baseline was recorded with the polytetrafluoroethylene (PTFE) reference disk covering the reflectance port. Data were collected at a scan rate of 600 nm/min with a data interval of 1.0 nm, a signal band width of 2.0 nm, and signal-averaging time of 0.1 s in the UV-VIS range.

3. Results

3.1. XRD results of Al-doped ZnO on GaAs substrate

XRD studies were used to analyze the growth orientation of the annealed ZnO:Al thin film at different annealing temperatures. PFCVAD ZnO:Al film was annealed in air at temperatures of 500 °C and 600 °C with 1 h annealing times. The X-ray diffraction patterns for both annealing temperatures are given in Figure 1.

The bottom graph belongs to the annealing at 500 °C for 1 h and the upper graph belongs to the annealing at 600 °C. It is clear from the XRD scans that we have amorphous features for ZnO:Al film annealed at 500 °C while ZnO:Al film annealed at 600 °C shows crystallinity for (100) and (002) orientations at around 32° and 34°, respectively. This is in agreement with the literature, where as-grown films showing amorphous features become crystalline after annealing [30].

3.2. XPS results of Al-doped ZnO on GaAs substrate

In this study, the chemical state of ZnO:Al (AZO) film was carried out by XPS. With the XPS analysis we measured the Zn2p, Ols, Al2p, Ga3d, and As3d core level spectra. The spectra were quantified using sensitivity factors after linear background subtraction and fitting using Gaussians functions, Lorentzian functions, or both with a weight factor using XPSPEAK41 software.

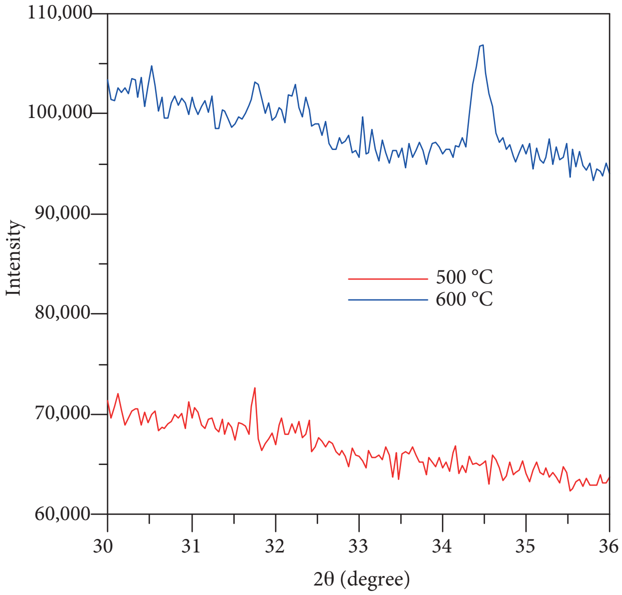

Figure 1. XRD spectrum of the ZnO:Al film annealed at 500 °C and 600 °C.

Photoelectron peaks in the XPS spectra of Zn2p, Ols, Al2p, Ga3d, and As3d were obtained for the annealed film at 500 °C. The AZO thin film is shown in Figures 2a–2e. The binding energies for all spectra were calibrated by taking the C1s peak, which has binding energy at 284.6 eV, as the reference.

Prominent peaks belonging to Zn and O are clearly seen in these graphs. Binding energies of Zn2p$_{3/2}$ and Zn2p$_{1/2}$ were observed at 1021.85 eV and 1044.82 eV, which is the same value of its natural form for metallic Zn (Figure 2a) [14].

In Figure 2b, we describe the O1s photoelectron spectra for AZO on GaAs substrate. The XPS spectra of the O1s core level were deconvolved into 2 components using XPSPEAK41 software and the profile of each peak was taken as an 80% Lorentzian and 20% Gaussian mixed function. Peaks at the binding energies of 530.2 eV and 531.8 eV were detected in the O1s region.

Table.

	Peak position (eV)	FWHM (eV)
Zn2p	1021.85	1.89
	1044.9	2.45
O1s	530.2	1.86
	531.8	1.83
Al2p	74.4	2.13
	76.7	4.37
Ga3d	22.75	4.08
As3d	44.80	2.06

In the Table, the corresponding fitting of the O1s spectra is given. In this study, the low binding energy component is centered at 530.2 eV. This component is attributed to the O^{2-} ions on the wurtzite structure of the hexagonal Zn^{2+} ion array, which are surrounded by zinc (or substitutional Al) atoms with their full supplement of nearest-neighbor O^{2-} ions. Therefore, the 530.2 eV peak of the O1s spectrum can be attributed to the Zn–O bonds [31–34].

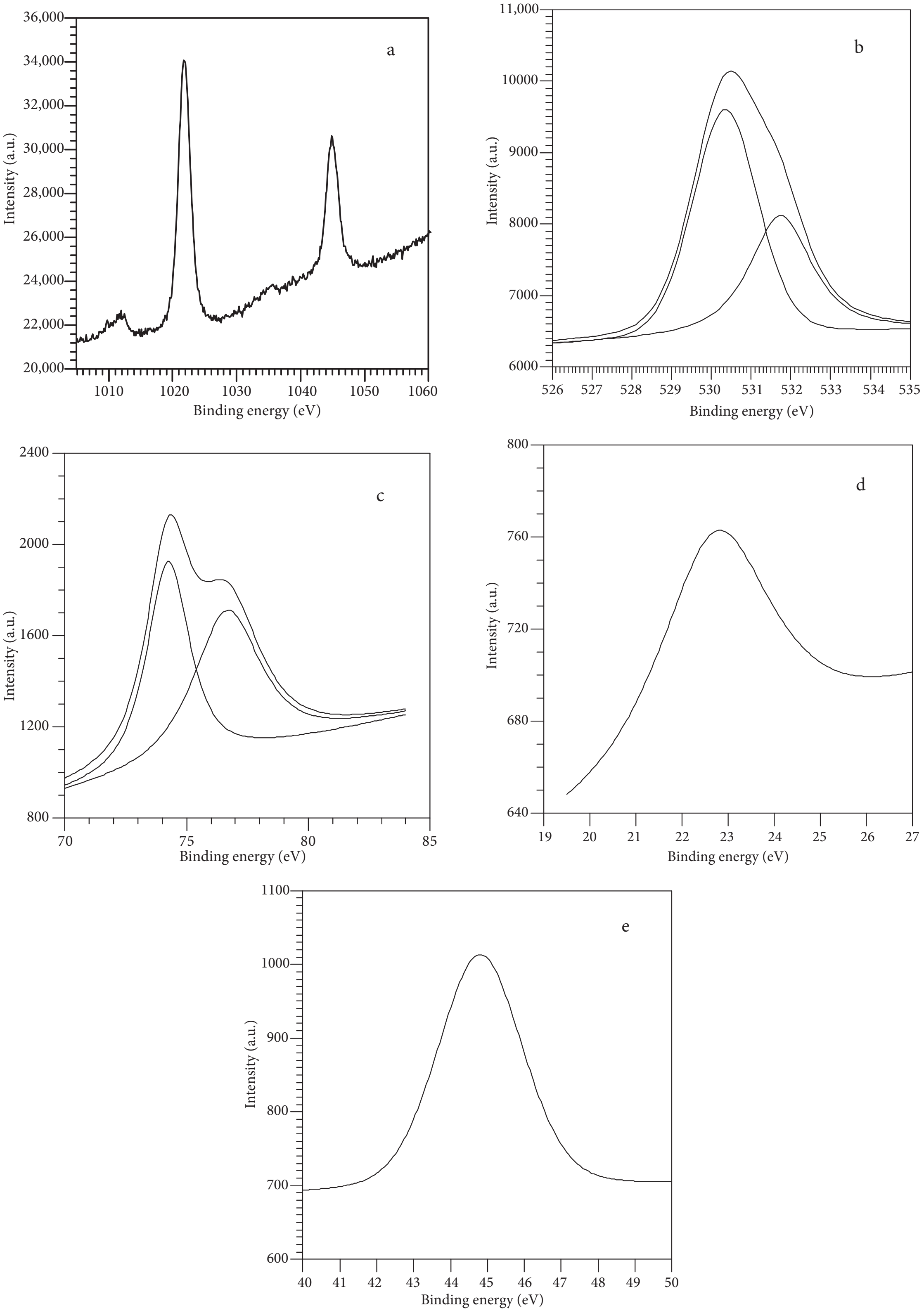

Figure 2. a) Zn2p, b) O1s, c) Al2p, d) Ga3d, and e) As3d photoelectron peaks in the XPS spectrum of the ZnO:Al film annealed at 500 °C.

The higher binding energy component is centered at 531.8 eV. It is usually attributed to chemisorbed or dissociated oxygen or OH species on the surface of the ZnO thin film, such as adsorbed H_2O or adsorbed O_2 [33–35].

In Figure 2c, we describe the Al2p photoelectron spectra for AZO on GaAs substrate. The XPS spectra of the Al2p core level were deconvolved into 2 components. The low bonding energy component centered at 74.4 eV may be due to the peak position of stoichiometric Al_2O_3 [33,36]. The bonding energy component centered at 76.7 eV may be due to the AlO(OH) [37].

The film has some peaks coming from the substrates, which are related to Ga2O3 and As2O3 photoelectron peaks at binding energies 22.75 eV and 44.80 eV (Figures 2d and 2e) [38].

3.3. Optical results of Al-doped ZnO on GaAs substrate

3.3.1. UV-VIS diffuse reflectance measurement

The optical properties of ZnO:Al grown on GaAs substrate were studied using a Varian Carry 5000 model UV-VIS-NIR spectrophotometer with an integrating sphere, using PTFE as the reference disk. Diffuse reflectance spectra were taken in the range of 200–800 nm and in air at room temperature.

The diffuse reflectance of the sample is related to the Kubelka–Munk function $F(R)$. Diffuse reflectance data were transformed using Kubelka–Munk function by the relation

$$F\,(R) = \frac{(1 - R)^2}{2R},$$

where R is the diffuse reflectance of the sample [39,40]. The Kubelka–Munk theory allows us to calculate the energy gap of the thin films on nontransparent substrates. According to graph of $F(R)$ versus energy values (Figure 3) the UV-absorption band of the ZnO:Al was around 360–380 nm.

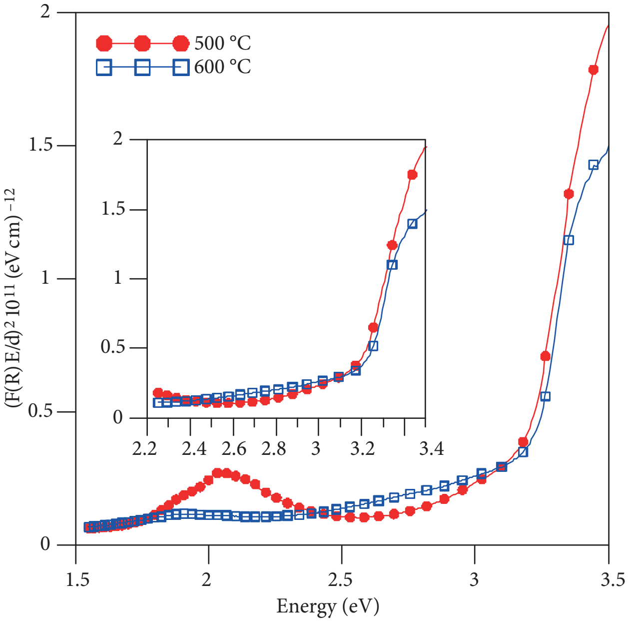

Figure 3. $(F(R)E/\mathrm{d})^2$ against photon energy (E) of the ZnO:Al film annealed at 500 °C and 600 °C for 1 h.

The energy band gap of Al-doped ZnO thin film was calculated by plotting the square of the Kubelka–Munk function versus energy (Figure 3). Extrapolating the linear portion of the curve onto the x-axis gives the energy band gap of the films. The band gap found by this method was 3.190 eV and 3.195 eV for film annealed at 500 °C and 600 °C, respectively. As a result, we conclude that the band gap of PFCVAD-grown ZnO:Al film annealed in air was substantially unaffected.

4. Conclusion

ZnO:Al thin film of thickness 408 nm was deposited on GaAs substrate by PFCVAD system. From XRD studies, we see no crystallinity for the 500 °C sample, but ZnO:Al film annealed at 600 °C shows (100) and (002) peaks. From optical properties, ZnO:Al film annealed in air was found to be substantially unaffected. Binding energies of Zn2p$_{3/2}$ and Zn2p$_{1/2}$ were observed at 1021.85 eV and 1044.82 eV, which is the same value of its natural form for metallic Zn. The peaks at the binding energies of 530.2 eV and 531.8 eV were detected in the O1s region. We described the Al2p photoelectron spectra for AZO on GaAs substrate. The XPS spectra of the Al2p core level were deconvolved into 2 components. Binding energies of Al2p were observed at 74.4 eV and 76.7 eV.

Acknowledgments

This research was supported by the Scientific Research Project Fund of Cumhuriyet University under project number F-320.

References

[1] Grundmann, M.; Rahm, A.; Nobis, T.; Lorenz, M.; Czekalla, C.; Evgeni, M. K.; Lenzner, J.; Boukos, N.; Travlos, A. In *Handbook of Self Assembled Semiconductor Nanostructures for Novel Devices in Photonics and Electronics*; Henini, M., Ed. Elsevier: Amsterdam, 2008, pp. 293–319.

[2] Gu, X. Q.; Zhu, L. P.; Cao, L.; Ye, Z. Z.; He, H. P.; Chu, P. K. *Mat. Sci. Semicond. Process.* **2011**, *14*, 48–51.

[3] Hwang, D. K.; Oh, M. S.; Lim, J. H.; Park, S. J. *J. Phys. D Appl. Phys.* **2007**, *40*, R387–R412.

[4] Ryu, Y. R.; Lubguban, J. A.; Lee, T. S.; White, H. W.; Jeong, T. S.; Youn, C. J.; Kim, B. J. *Appl. Phys. Lett.* **2007**, *90*, 131115-131115-3.

[5] Ezema, F. I.; Nwankwo, U. O. A. *J. Optoelectron. Biomed. Mat.* **2010**, *1*, 167–173.

[6] Mahmood, A.; Ahmed, N.; Raza, Q.; Khan, T. M.; Mehmood, M.; Hassan, M. M.; Mahmood, N. *Phys. Scr.* **2010**, *82*, 065801.

[7] Guillén, C.; Herrero, J. *Thin Solid Films* **2005**, *480–481*, 129–132.

[8] Emziane, M.; Durose, K.; Romeo, N.; Bosio, A.; Halliday, D. P. *Thin Solid Films* **2005**, *480*, 377–381.

[9] Li, Q. H.; Zhu, D.; Liu, W.; Liu, Y.; Ma, X. C. *Appl. Surface Sci.* **2008**, *254*, 2922–2926.

[10] Song, D.; Aberle, A. G.; Xia, J. *Appl. Surf. Sci.* **2002**, *195*, 291–296.

[11] Jiang, X.; Wong, F. L.; Fung, M. K.; Lee, S.T. *Appl. Phys. Lett.* **2003**, *83*, 1875–1877.

[12] Kim, H.; Horwitz, J. S.; Kushto, G. P.; Kafafi, Z. H.; Chrisey, D. B. *Appl. Phys. Lett.* **2001**, *79*, 284–286.

[13] Marotti, R. E.; Bojorge, C. D.; Broitman, E.; Cánepa, H. R.; Badán, J. A.; Dalchiele, E. A.; Gellman, A. J. *Thin Solid Films* **2008**, *517*, 1077–1080.

[14] Wang, F. H.; Chang, H. P.; Tseng, C. C.; Huang, C. C. *Surface & Coatings Technol.* **2011**, *205*, 5269–5277.

[15] Park, Y. S.; Kim, H. K. *Thin Solid Films* **2011**, *519*, 8018–8022.

[16] Wang, T.; Diao, X.; Wang, X. *Appl. Surface Sci.* **2011**, *257*, 9773–9779.

[17] Kumarakuru, H.; Cherns, D.; Fuge, G. M. *Surface & Coatings Technol.* **2011**, *205*, 5083–5087.

[18] Li, Z. Z.; Chen, Z. Z.; Huang, W.; Chang, S. H.; Ma, X. M. *Appl. Surface Sci.* **2011**, *257*, 8486–8489.

[19] Bahedi, K.; Addou, M.; Jouad, M. E.; Sofiani, Z.; Oauzzani, H. E.; Sahraoui, B. *Appl. Surface Sci.* **2011**, *257*, 8003–8005.

[20] Gao, M.; Wu, X.; Liu, J.; Liu, W. *Appl. Surface Sci.* **2011**, *257*, 6919–6922.

[21] Gao, F.; Yua, K. M.; Mendelsberga, R. J.; Andersa, A.; Walukiewicza, W. *Appl. Surface Sci.* **2011**, *257*, 7019–7022.

[22] Chandramohan, R.; Vijayan, T. A.; Arumugam, S.; Ramalingam, H. B.; Dhanasekaran, V.; Sundaram, K.; Mahalingam, T. *Mater. Sci. Eng. B* **2011**, *176*, 152–156.

[23] Xu, X. L.; Lau, S. P.; Tay, B. K. *Thin Solid Films* **2001**, *398–399*, 244–249.

[24] Wang, Y. G.; Lau, S. P.; Lee, H. W.; Yu, S. F.; Tay, B. K.; Zhang, X. H.; Tse, K. Y.; Hng, H. H..*J. Appl. Phys.* **2003**, *94*, 1597–1604.

[25] Takikawa, H.; Kimura, K.; Miyano, R.; Sakakibara, T. *Vacuum* **2002**, *65*, 433–438.

[26] David, T.; Goldsmith, S.; Boxman, R. L. *Thin Solid Films* **2004**, *447–448*, 61–67.

[27] Şenadım, E.; Kavak, H.; Esen, R. *J. Phys. Condens. Matter* **2006**, *186*, 6391–6400.

[28] Anders, S.; Anders, A.; Rubin, M.; Wang, Z.; Raoux, S.; Kong, F.; Brown, I. G. *Surf. Coat. Technol.* **1995**, *76/77*, 167–173.

[29] Şenadım Tüzemen, E.; Kavak, H.; Esen, R. *Phys. B Condens. Matter* **2007**, *390*, 366–372.

[30] Bruncko, J.; Vincze, A.; Netrvalova, M., Sutta, P.; Hasko, D.; Michalka, M. *Thin Solid Films* **2011**, *520*, 866–870.

[31] Cebulla, R.; Wendt, R.; Ellmer, K. *J. Appl. Phys.* **1998**, *83*, 1087–1095.

[32] Li, L.; Fang, L.; Zhou, X. J.; Liu, Z. Y.; Zhao, L.; Jiang, S. *J. Electron Spectrosc. Relat. Phenom.* **2009**, *173*, 7–11.

[33] Chen, M.; Wang, X.; Yu, Y. H.; Pei, Z. L.; Bai, X. D.; Sun, C.; Huang, R. F.; Wen, L. S. *Appl. Surf. Sci.* **2000**, *158*, 134–140.

[34] Prasada Rao, T.; Santhosh Kumar, M. C.; Safarulla, A.; Ganesan, V.; Barman, S. R.; Sanjeeviraja, C. *Phys. B* **2010**, *405*, 2226–2231.

[35] Moulder, J. F.; Stickel, W. F.; Sobol, P. E.; Bomben, K. D. *Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data*; Physical Electronics Division, Perkin-Elmer Corporation: Eden Prairie, MN, USA, 1995.

[36] Uma, K.; Rusop, M.; Soga, T.; Jimbo, T. *Jpn. J. Appl. Phys.* **2007**, *46*, 40–44.

[37] Lindsay, J. R.; Rose, H. J.; Swartz, W. E.; Watts, P. H.; Rayburn, K. A. *Appl. Spectrosc.* **1973**, *27*, 1–5.

[38] Mizokawa, Y.; Iwasaki, H.; Nishitani, R.; Nakamura, S. *J. Electron Spectrosc. Relat. Phenom.* **1978**, *14*, 129–141.

[39] Cimitan, S.; Albonetti, S.; Forni, L.; Peri, F.; Lazzari, D. *J. Colloid Interface Sci.* **2009**, *329*, 73–80.

[40] Saleh, R.; Prakoso, S. P.; Fishli, A. J. Magn. Magn. Mater. **2012**, *324*, 665–670.