ANALYSIS OF GLASSES COATED WITH Zn-Cr-Sn-O THIN FILMS BY PICOSECOND LASER-INDUCED BREAKDOWN SPECTROSCOPY AND TRANSMISSION SPECTROSCOPY

Q. Gao, Sh. Liu, J. Xiu*, Zh. Li, Y. Liu, H. Liu

Institute of Advanced Imaging and Data Mining, School of Physics and Optoelectronic Engineering, Shandong University of Technology,
Shandong Zibo, 255049, China; e-mail: xiujunshan@126.com; liuhq@sdut.edu.cn

Glasses coated with different thin film layers exhibit different optical properties. Thus, ZnO thin films with Sn and Cr admixture (ZCTO) were deposited on the glass substrate surface by radio frequency magnetron sputtering. Picosecond laser-induced breakdown spectroscopy (ps-LIBS) was applied to achieve the rapid analysis of the doping elements in the ZCTO thin film. In addition, the transmittance spectra of the glasses coated with ZCTO thin films deposited at different sputtering times were recorded with the UV-VIS-NIR spectrophotometer. A red shift of 45±2 nm was observed in the absorption edge of the transmittance curve (UV wave band from 330 to 400 nm), which was highlighted with increase in the sputtering time. Moreover, the optical band gaps of ZCTO thin films were determined, which overall were larger than those of ZnO thin films only. Lastly, the relationships between the LIBS analysis and the optical properties of the glass samples were established. As revealed from the results, ps-LIBS can control or assist in the fabrication of high performance ZCTO thin films employed for glass production.

Keywords: *Zn-Cr-Sn-O thin film, picosecond laser-induced breakdown spectroscopy, glass, optical properties.*

АНАЛИЗ СТЕКОЛ, ПОКРЫТЫХ ТОНКИМИ ПЛЕНКАМИ Zn-Cr-Sn-O, МЕТОДАМИ СПЕКТРОСКОПИИ ЛАЗЕРНО-ИНДУЦИРОВАННОЙ ПЛАЗМЫ С ПИКОСЕКУНДНЫМ ВОЗБУЖДЕНИЕМ И СПЕКТРОСКОПИИ ПРОПУСКАНИЯ

Q. Gao, Sh. Liu, J. Xiu*, Zh. Li, Y. Liu, H. Liu

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Школа физики и оптоэлектронной инженерии Шаньдунского технологического университета,
Шаньдун Цзыбо, 255049, Китай; e-mail: xiujunshan@126.com; liuhq@sdut.edu.cn

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Тонкие пленки ZnO с примесью Sn и Cr (ZCTO) наносились на поверхность стеклянной подложки методом радиочастотного магнетронного распыления. Спектроскопия лазерно-индуцированной плазмы с пикосекундным возбуждением (ps-LIBS) применена для быстрого анализа легирующих элементов в тонкой пленке ZCTO. Спектры пропускания стекол, покрытых тонкими пленками ZCTO, осажденными при разном времени распыления, зарегистрированы с помощью спектрофотометра UV-VIS-NIR. Красный сдвиг на 45±2 нм, отмеченный на крае поглощения спектра пропускания (УФ-полоса 330–400 нм), выделялся с увеличением времени распыления. Определены ширины оптических запрещенных зон тонких пленок ZCTO, которые оказались большими, чем у тонких пленок ZnO. Установлена связь между LIBS-сигналом и оптическими свойствами образцов стекла.

Ключевые слова: *тонкая пленка Zn-Cr-Sn-O, спектроскопия лазерно-индуцированной плазмы с пикосекундным возбуждением, стекло, оптические свойства.*

Introduction. Zinc oxide (ZnO) thin films doped with suitable elements as transparent conductive oxide thin films (TCOs) have been applied extensively in numerous devices (e.g., photoconductive ultraviolet detectors [1], solar cell [2, 3], light emitting devices [4], and thin film transistors [5, 6]). Overall, ZnO thin films doped with aluminum [7], gallium [8], tin [9–11], and chromium [12, 13] are capable of acting as extrinsic elements to produce *n*-type ZnO, as well as altering the electrical conductivity and optical properties by varying their concentrations. Among the mentioned metals, Sn and Cr have been commonly adopted to improve the optical and optoelectronic properties of substrates coated with ZnO thin films. Earlier, a single element such as Sn or Cr was added to ZnO thin film to alter the properties of the substrates. In the present study, ZnO thin films doped with Sn and Cr together were prepared and deposited on glass substrates. Thus, the optical properties of the glass substrates were improved.

Numerous available analytical technologies have been applied to the analysis of elements in thin films, namely, X-ray fluorescence (XRF), glow discharge optical emission spectroscopy (GD-OES), and energy dispersive X-ray spectroscopy (EDS). However, they are performed on highly complex and expensive equipment and require expertise and reliable sample preparation, which is time-consuming. For the reasons mentioned above, these techniques increase the characterization cost of the thin film.

Laser induced breakdown spectroscopy (LIBS) has been widely used in different fields and received more and more attention over the past few decades [14–19]. Specifically, many achievements have been made in thin film analysis with the LIBS technology [19–22]. However, the existing studies mainly focus on the experimental parameter optimization of LIBS (laser wavelength), the quantitative analysis, and the plasma emission. The relationships between the optical properties of the substrates coated with thin films and the emission intensities of elements in thin films have not been studied further.

In our previous work, we analyzed the elements in thin films by ns- and ps-LIBS, such as titanium oxide thin films [23], aluminum-indium-tin-oxide thin films [24], and copper-indium-gallium-selenium thin films [25]. In the present study, ZnO thin films with Sn and Cr admixture were prepared using one-step radio frequency (RF) magnetron sputtering. Moreover, the Zn-Cr-Sn-O thin films (ZCTO) were coated on the surface of the glass substrate. Subsequently, ps-LIBS was performed to analyze the elements in the ZCTO thin film, and transmittance spectroscopy was employed to record the transmittance of the glasses coated with different ZCTO thin films. Lastly, the relationships between LIBS analysis and the optical properties of the glass samples were discussed, and the feasibility and availability of ps-LIBS to control or assist in fabricating high-performance ZCTO thin films applied to glass was verified.

Experimental. ZCTO thin films were prepared at room temperature using RF magnetron sputtering from a zinc oxide target (purity 99.99 wt.%, Zhongnuo New Material, China) doped with chromium oxide and tin oxide at a size of 75×5 mm. The content ratio of Zn, Cr, and Sn in the zinc oxide target was 80:2:18 at%. Normal soda-lime glasses (SLG) used as substrates were put into the vacuum chamber. The distance from target to substrate was 150 mm, and the sputtering medium Ar (purity, 99.99 wt.%) exhibited a flow rate of 20 sc/cm under work pressure of 3.0 Pa and sputtering power of 90 W. In our work, a number of ZCTO thin film samples were deposited in the range of sputtering times from 5 to 25 min. The presputtering was completed before the deposition. EDS (Oxford INCA Energy, England) was used to analyze the samples. Table 1 listed the EDS values of ZCTO thin film samples obtained at sputtering times ranging from 5 to 25 min. The ratios of each element in the table were the mean values of the EDS measurements at four different sample locations. Moreover, the relative content ratios of Cr/Zn and Sn/Zn in the ZCTO thin films were calculated, as shown in Table 1. Obviously, the atomic concentrations in all the ZCTO thin films samples were not consistent with those in the target samples in the range of the sputtering time. For the ZCTO targets, a nonuniform distribution of different elements deposited on the surface of the glass substrate might occur under different sputtering times because of different activities of the metal elements or the heating of the deposition environment.

TABLE 1. EDS Values (Atomic concentration, at. %) of Different ZCTO Thin Films Obtained at Sputtering Times Ranging from 5 to 25 min

Sputtering time, min	Zn	Cr	Sn	Cr/Zn	Sn/Zn
5	83.25	1.68	15.07	0.0202	0.180
10	82.46	1.72	15.82	0.0209	0.192
15	80.84	1.82	17.34	0.0225	0.215
20	79.56	2.12	18.32	0.0266	0.230
25	78.48	2.25	19.27	0.0287	0.246

A typical LIBS setup with picosecond laser pulses was used in this study, as shown in Fig. 1. Its specific description is presented elsewhere [24]. In brief, the picosecond laser pulses operating at 1064 nm under pulse duration of 350 ps, repetition rate of 500 Hz, and pulse energy of 122 μJ were focused on the surfaceof the ZCTO thin film by a combined lens (L1) with beam expanding and beam focusing (focal length 35 mm). The ZCTO thin film sample was placed on a motorized micrometric 3-D displacement stage. To avoid the glass substrate from being directly ablated under the ZCTO thin film, the focal point of the laser pulse was set over the sample surface with a shift of nearly 0.2 mm. The plasma emissions were collected into the fiber at a 45°-angle over the plasma by two lenses with focal lengths of 35 (L2) and 16 mm (L3), respectively. The output of the fiber was connected to the entrance of a portable optical fiber spectrometer (AvaSpec-Mini2048CL-SOT8, Avantes Technology) under a spectral bandwidth from 240 to 415 nm with a spectral resolution of 0.1 nm when the slit was 10 μm. The integration time of the spectrometer was set to 500 ms, and the horizontal moving speed and single moving distance of the displacement stage were set to 25 mm/s and 12.5 mm, respectively. Note that 250 laser pulses were focused uniformly on the surface of the ZCTO thin film layer with a distance of 12.5 mm (Fig. 1). The ablation thin film thickness of the ZCTO thin film layer with a single laser shot can be estimated as nearly 55±5 nm, corresponding to the emissions of samples ablated between the fourth and fifth laser shot, as explained in [26]. All the experimental conditions were kept constant for all ZCTO thin films samples. Furthermore, the plasma emissions induced from 250 laser pulses were accumulated using a spectrometer with a detection width of 500 ms. In our experiment, the plasma temperature was as low as about 5000 K [24]; thus, the detection delay time of the spectrograph was set to minimum to achieve high plasma emission intensity.

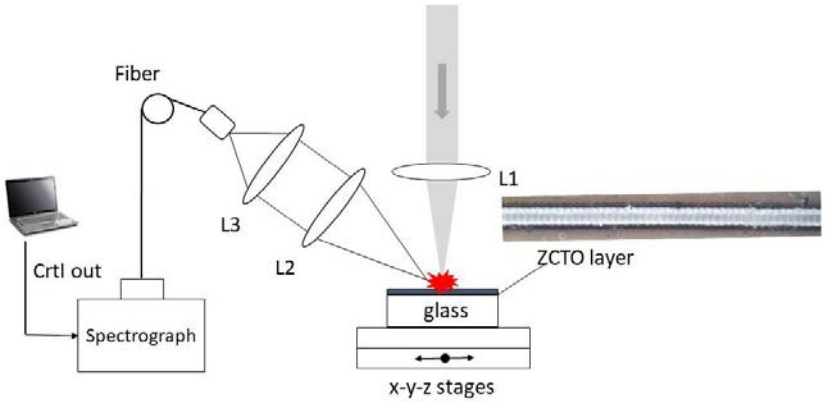

Fig. 1. The LIBS setup for ZCTO thin film analysis.

Results and discussion. *LIBS raw spectra and spectral lines selection*. To effectively analyze the ZCTO thin film, the spectral lines of the interesting elements in the ZCTO thin film should be selected. Figure 2 presents a LIBS spectrum recorded for a ZCTO thin film sample deposited at sputtering time of 20 min. The film thickness of the ZCTO thin layer reached approximately 300 nm, as measured with a film thickness gauge. The spectrum presented was in the most interesting spectral range from 250 to 400 nm, and the inset illustrated the specific spectrum from 280 to 290 nm and 356 to 362 nm. Emission lines from Zn, Cr, and Sn in ZCTO thin film can be identified and observed in the spectrum, as listed in Table 2. In this spectrum, the CN bands around 358 nm could not be observed (Fig. 2), although the laser pulses were focused slightly above the sample surface with a shift of 0.2 mm. Therefore, it was suggested that the ambient atmospheric air could not be ablated at this focused distance in the experiment. Furthermore, the calcium emissions (Ca I 393.63 nm and Ca I 396.85 nm) from the glass substrate were not observed in this spectrum (Fig. 2), indicating that the ZCTO thin film layer was only ablated and the glass substrate was not damaged. Therefore, it was demonstrated that the distance between lens L1 and the surface of the ZCTO thin film samples was suitable.

The concentrations of Sn and Cr in the ZCTO thin film could significantly affect the optical properties of the thin film, so Sn and Cr were set as the analytical elements here. A suitable spectral line should be selected for the Sn and Cr to be detected. In the spectral range shown in Fig. 1, nine spectral lines of Sn I, three spectral lines of Cr I, and seven spectral lines of Cr II were observed, as listed in Table 2. The selected lines were first relatively intense under the given ablation and detection conditions, which maximally avoided

TABLE 2. List of Observed Spectral Lines of Elements in the ZCTO Thin Film

Element	Number of lines	Wavelength at the peak positions, nm
Sn I	9	270.65, 283.99, 286.33, 300.91, 303.41, 317.51, 333.06, 380.10, 326.23
Zn I	3	328.23, 330.26, 334.50
Zn II	1	255.96
Cr I	3	357.87, 359.35, 360.53
Cr II	7	283.54, 284.26, 284.99, 286.31,311.99, 312.40, 313.12

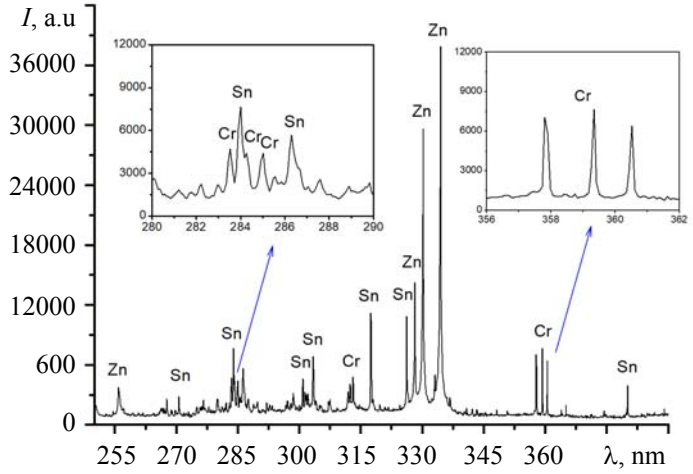

Fig. 2. The LIBS spectrum of the ZCTO thin film deposited with sputtering time of 20 min. The inset shows the detailed spectrum for the elements of interest.

interference from other spectral features. Five spectral lines of Sn I 283.99, 303.41, 317.51, 326.23, and 380.10 nm were presented with relative intensities of respectively 13,000, 10,000, 15,000, 15,000, and 6,900, according to the NIST atomic spectra database [27]. We could see that the Sn I 283.88 nm with the relative intensity was overlapped and disturbed with the Cr emissions, as suggested from the inset of Fig. 2, and the Sn I 326.23 nm was also disturbed with the Zn emissions. Furthermore, three discrete spectral lines of Cr I 357.87, 359.35, and 360.53 nm were presented with relative intensities of 1380, 1450, and 1240, respectively, according to the NIST atomic spectra database [27]. Accordingly, the Sn I 317.51 nm and Cr I 359.35 nm were taken as the analytical spectral line. The signal-to-noise ratio (SNR) of lines Sn I 317.51 nm and Cr I 359.35 nm could be calculated as more than 50.

The LIBS intensity evolutions of Sn and Cr in the ZCTO thin films deposited at various sputtering times. Since the Sn and Cr concentrations in TCO thin films were recognized to be significant in controlling the optical band gap of TCO thin films [9, 10, 12, 13], the LIBS intensities of Sn and Cr could predict their concentration in thin films. Figure 3 showed the LIBS intensity ratio evolutions of Sn/Zn and Cr/Zn in ZCTO thin films deposited at different sputtering times, in which the LIBS intensity of Zn I 334.50 nm was exploited

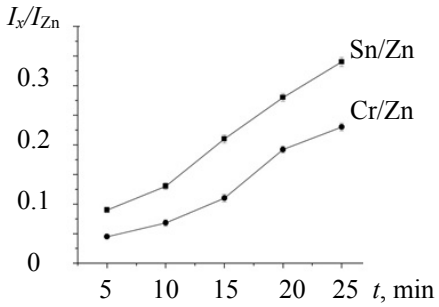

Fig. 3. The LIBS intensity ratio evolutions of Sn/Zn and Cr/Zn in the ZCTO thin film deposited at various sputtering times.

for the normalization. In Fig. 3, each data point represented the mean value of seven replicate measurements, and the error bars indicated their associated standard deviations. As observed from the results, thespectral line intensities of Sn I 317.51 nm and Cr I 359.35 nm increased with increase in the sputtering time. It was therefore suggested that the concentrations of Sn and Cr in ZCTO thin films also increased. The reason was that more Sn and Cr atoms were sputtered on the glass substrate from the target with increase in the sputtering time with RF magnetron sputtering. The LIBS intensity ratio evolutions of Sn/Zn and Cr/Zn were consistent with those obtained from the EDS data shown in Table 1.

Optical properties of the glasses coated with ZCTO thin films. When the glass substrate was coated with the ZCTO thin film layer, its optical properties were changed in response to the concentration variations of the elements in the ZCTO thin film, such as Sn and Cr. To determine the optical properties of the glass coated with different ZCTO thin film layers, the corresponding transmittance spectra were recorded with the UV-VIS-NIR spectrophotometer. Figure 4 showed the five transmittance spectra of the glasses coated with ZCTO thin films deposited at different sputtering times. The spectral range was set from 330 to 800 nm, covering different wave bands of UV-VIS-NIR.

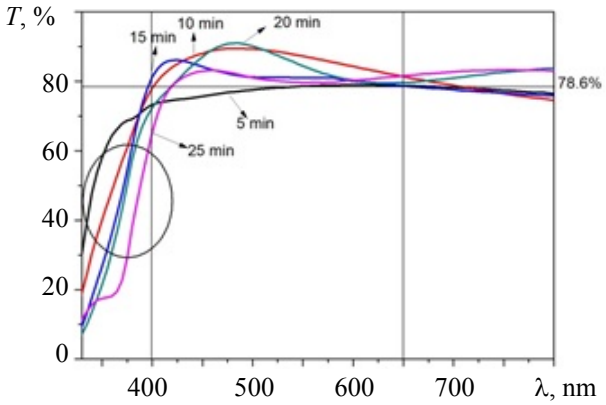

Fig. 4. The transmittance spectra of the glasses coated with ZCTO thin films deposited at various sputtering times measured by the UV-VIS-NIR spectrophotometer.

In Fig. 4, we observe that the transmittances of the glasses were all >78.6% under the visible spectral range from 400 to 650 nm, except for the one coated with the ZCTO thin film deposited at a sputtering time of 5 min. This was probably because the ZCTO thin film layer might not be formed uniformly on the surface of the glass substrate at a sputtering time of 5min. Moreover, in Fig. 4, a red shift of 45±2 nm in the absorption edge of the transmittance curve (the circular region of transmission curves) was highlighted as the increase in the sputtering time, which resulted from the increase in the Sn and Cr concentrations in ZCTO thin films. In the spectral range from 400 to 650 nm (VIS wave band), the average transmittances of the glasses coated with ZCTO thin films deposited at a sputtering time of 10, 15, and 20 min were higher than those at a sputtering time of 5 and 25 min. Although the concentrations of Sn and Cr in the ZCTO thin film were maximum due to the longest sputtering time (25 min), the thickness of the thin film layer might be the thickest, so both the ultraviolet and visible light transmittances decreased. However, the average transmittances in the spectral range from 700 to 800 nm (NIR wave band) were lower than those under the visible spectral range. This indicated that the infrared reflection and absorption effect of the glasses coated with ZCTO thin films increased corresponding to the glasses only.

To clarify the exhibited optical properties of the glasses coated with ZCTO thin films, the optical band gap (E_g) was calculated by a linear plot of (hv^2) versus photon energy curve to the intercept on the horizontal photon energy axis [28], which was converted from the circular region of transmission curves shown in Fig. 4. According to this method, the determined E_g values of five ZCTO thin films deposited at various sputtering times (i.e., 5, 10, 15, 20, and 25 min) reached 3.866, 3.786, 3.717, 3.697, and 3.601 eV, respectively, which were overall larger than that of the ZnO thin film (3.37 eV). This indicated that the variable concentrations of Sn and Cr in ZCTO thin films could alter the optical band gaps of ZCTO thin films, thereby affecting the transmittance of the glasses coated with these ZCTO thin films.

With increase in the sputtering time from 5 to 25 min, the band gap decreased from 3.866 to 3.601 eV. This shows that, by adding the dopant, the increasing donor electrons lower their energy level below the conduction band. Also, the relative concentration ratios of Sn/Zn and Cr/Zn increased linearly with increase in the sputtering time, as shown in Fig. 3. It was therefore indicated that excess Sn^{4+} and Cr^{3+} had not replaced Zn^{2+} ions but occupied the interstitial sites, which could not liberate the free electrons. The free charge carriers increased significantly with high concentrations of Sn doping and the corresponding downward shift of the Fermi level to a value below the band edge [29]. In fact, the variation of the band gap of the ZnO thin films doped with Sn and Cr showed an association with the doping concentration of Sn and Cr, as well as with the annealing temperature, the film deposition method, and the precursor of Sn and Cr, etc. [30–33].

Figure 5 presents the optical band gap evolutions of ZCTO thin films with the LIBS intensity ratios of Sn/Zn (a) and Cr/Zn (b) in the ZCTO thin films deposited at different sputtering times. It indicates that the optical band gap of the thin film can be exhibited by the LIBS spectral line intensity ratios of Sn/Zn and Cr/Zn in the thin film, which can also determine their optical properties corresponding to the transmittance of the glass substrates. In further work, the relationships between the heating effect of ZCTO thin films and LIBS analysis will be determined.

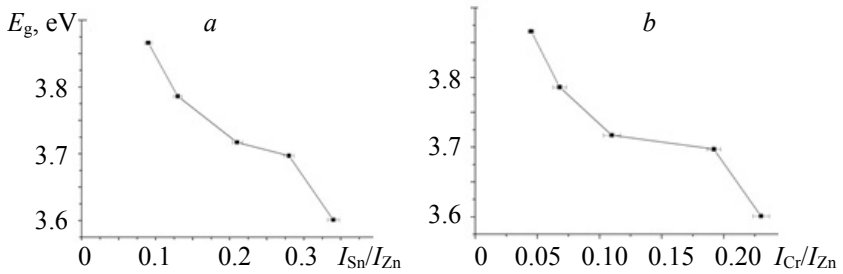

Fig. 5. The optical band gaps of ZCTO thin films with LIBS intensity ratios of Sn (a) and Cr (b) in ZCTO thin films deposited at different sputtering times.

Conclusions. ZnO thin films with the Sn and Cr admixture were prepared using the one-step radiofrequency magnetron sputtering method. The Zn-Cr-Sn-O thin films (ZCTO) were covered on the surface of the glass substrate. Ps-LIBS was performed to analyze the elements in the ZCTO thin films, including the selection of analytical lines and elemental emissions in thin films. To obtain the optical properties of the glasses coated with ZCTO thin film layers, the corresponding transmittance spectra were recorded with the UV-VIS-NIR spectrophotometer. A red shift of 45±2 nm was identified in the absorption edge of the transmittance curve (UV wave band from 330 to 400 nm), which was highlighted as the increase in sputtering time, and the infrared reflection and absorption effect of the glass coated with the ZCTO thin film increased corresponding to the glass only. Lastly, the optical band gap of the ZCTO thin film could be exhibited by the LIBS spectral line intensity ratios of Sn and Cr in the thin film, which could also determine the optical properties corresponding to the transmittance of the glass substrate.

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REFERENCES

1. K. Singh, I. Rawal, N. Sharma, P. Gautam, R. Dhar, *Mater. Sci. Semicond. Proc*., **95**, 7–19 (2019).
2. G. S. Lin, C.Y. Li, K. C. Huang, M. P. Houng, *Mater. Chem. Phys*., **160**, 264–270 (2015).
3. S. J. Lee, S. Kim, D. C. Lim, D. H. Kim, S. Nahm, S. H. Han, *J. Alloy Compd*., **777**, 717–722 (2019).
4. Z. Zang, X. Zeng, J. Du, M. Wang, X. Tang, *Opt. Lett*., **41**, 3463–3466 (2016).
5. A. Abliz, L. Xu, D. Wan, H. Duan, J. Wang, C. Wang, S. Luo, C. Liu, *Appl. Surf. Sci*., **475**, 565–570 (2019).
6. P. Ray, V. R. Rao, *Appl. Phys. Lett*., **102**, 064101 (2013).
7. B. E. Sernelius, K. F. Berggren, Z. C. Jin, I. Hamberg, C. G. Granqvist, *Phys. Rev. B*, **37**, 10244–10248 (1988).

8. L. J. Mandalapu, F. X. Xiu, Z. Yang, J. L. Liu, *Solid State Electron*., **51**, 1014–1017 (2007).
9. S. Q. Li, C. B. Yao, Y. Han, G. Q. Jiang, Y. Cai, H. T. Yin, W. J. Sun, *Opt. Mater*., **96**, 109329 (2019).
10. Y. Andolsi, F. Chaabouni, M. Abaab, *J. Mater. Sci.: Mater. Electron*., **28**, 8347–8358 (2017).
11. L. H. Xu, G. G. Zheng, F. G. Xian, J. Su, *Mater. Chem. Phys*., **229**, 215–225 (2019).
12. S. Singh, E. S. Kumar, M. S. R. Rao, *Scr. Mater*., **58**, 866–869 (2008).
13. Y. Andolsi, F. Chaabouni, *J. Alloys Comp*., **806**, 152739 (2019).
14. P. Celio, C. Juliana, M. C. S. Lucas, B. G. Fabinao, *J. Braz. Chem. Soc*., **18**, 463–512 (2007).
15. A. De Giacomo, M. Dell'Aglio, O. De Pascale, M. Capitelli, *Spectrochim. Acta B*, **62**, 721–738 (2007).
16. Y. Tian, B.Y. Xue, J. J. Song, Y. Lu, R. E. Zheng. *Appl. Phys. Lett*., **109**, 061104 (2016).
17. J. S. Xiu, L. L. Dong, Y. Y. Liu, J. Y. Li, *J. Appl. Spectrosc*., **86**, 43–49 (2019).
18. V. S. Burakov, N. V. Tarasenko, M. I. Nedelko, V. N. Kononovb, N. N. Vasilevb, S. N. Isakov, *Spectrochim. Acta B*, **64**, 141–146 (2009).
19. J. Zhang, K. Dong, Q. Fan, F. Zhao, X. Li, J. Chen, Q. Guo, *Appl. Laser*, **32**, 420–423 (2012).
20. J. H. In, C. K. Kim, S. H. Lee, S. S. Hee, *J. Anal. At. Spectrom*., **28**, 890–900 (2013).
21. N. Haustrup, G. M. O'Connor, *Appl. Surf. Sci*., **302**, 1–5 (2014).
22. T. O. Nagy, U. Pacher, H. Pöhl, W. Kautek, *Appl. Surf. Sci*., **302**, 189–193 (2014).
23. J. S. Xiu, S. M. Liu, M. L. Sun, L. L. Dong, *Appl. Opt*., **57**, 404–408 (2018).
24. S. M. Liu, Q. Gao, J. S. Xiu, Z. Li, Y. Y. Liu, *Spectrochim. Acta B*, **160**, 105684 (2019).
25. J. S. Xiu, S. M. Liu, S. G. Fu, T. Wang, M. X. Meng, Y. Y. Liu, *Appl. Opt*., **58**, 1040–1047 (2019).
26. S. M. Liu, Q. Gao, L. L. Dong, J. S. Xiu, Y. Y. Liu, *Opt. Commun*., **462**, 125369 (2020).
27. https://physics.nist.gov/PhysRefData/ASD/lines_form.html
28. G. Adamopoulos, S. Thomas, D. D. C. Bradley, M. A. McLachlan, T. D. Anthopoulos, *Appl. Phys. Lett*., **98**, 123503 (2011).
29. R. Beura, R. Pachaiappan, P. Thangadurai, *Appl. Surf. Sci*., **433**, 887–898 (2018).
30. M. Ajili, M. Castagne, N. K. Turki, *Superlattice Microstruct*., **53**, 213–222 (2013).
31. H. Aydin, H. M. El-Nasser, C. Aydin, A. A. Al-Ghamdi, F. Yakuphanoglu, *Appl. Surf. Sci*., **350**, 109–114 (2015).
32. K. Ravichandran, M. Vasanthi, K. Thirumurugan, B. Sakthivel, K. Karthika, *Opt. Mater*., **37**, 59–64 (2014).
33. N. H. Sheeba, S. C. Vattappalam, J. Naduvath, P. V. Sreenivasan, S. Mathew, R. K. Philip, *Chem. Phys. Lett.*, **635**, 290–294 (2015).