

Cite this: *J. Mater. Chem. C*, 2017,
5, 7598

Performance improvement of a ZnMgO ultraviolet detector by chemical treatment with hydrogen peroxide

Yongxue Zhu,^{ab} Kewei Liu,^{*a} Xiao Wang,^{ab} Jialin Yang,^{ab} Xing Chen,^a Xiuhua Xie,^a Binghui Li^a and Dezhen Shen^{*a}

Herein, ZnMgO thin film ultraviolet (UV) photodetectors based on metal–semiconductor–metal structure were fabricated on a-plane sapphire substrates by plasma-assisted molecular beam epitaxy. The effect of H₂O₂ solution treatment on the properties of the ZnMgO thin film and its UV photodetectors was investigated. After immersing the ZnMgO UV photodetector in a H₂O₂ solution at 100 °C for 3 min, the dark current of the device was reduced by more than one order of magnitude under 1 V bias, whereas the responsivity was slightly decreased. More interestingly, the response speed became much quicker and insensitive to the atmosphere after the treatment of the photodetector with H₂O₂ solution, which can be attributed to the reduction in the oxygen vacancy defects. Our findings may provide a promising approach for improving the performance of photodetectors.

Received 2nd June 2017,
Accepted 4th July 2017

DOI: 10.1039/c7tc02425h

rsc.li/materials-c

Introduction

Ultraviolet (UV) photodetectors have received significant attention due to their widely potential applications such as in flame detection, space-to-space communication, missile plume detection, astronomy and biological research.^{1–4} ZnO, as a direct wide-band-gap semiconductor (~3.37 eV), has been regarded as one of the most promising materials for the fabrication of UV photodetectors due to its low defect density, high radiation hardness, low cost, and environmental friendliness. Moreover, the alloying of ZnO with MgO to make ZnMgO can continually increase the band gap from ~3.37 eV to ~7.8 eV, which allows the detection of both solar blind and visible blind UV radiation.⁵ To date, various ZnO-based UV photodetectors have been realized with different device structures such as p–n junction, Schottky junction, metal–semiconductor–metal (MSM) structure, and nanosensor.^{6–10} According to the previous reports, the electrical and the optoelectronic properties of these devices are significantly dependent on the quality of ZnO-based semiconductor materials.^{11,12} Especially, ZnO exhibits a strong chemisorption/desorption behavior through surface processes; thus, the performance of ZnO-based UV photodetectors is strongly affected by the surface states of ZnO.^{13,14} For example, the slow O₂ adsorption/desorption processes on the surface of ZnO could lead to the

long rise/decay time of bare ZnO UV photodetectors.^{12,15} Moreover, the responsivity and the dark current of ZnO-based UV photodetectors are usually affected by H₂O/O₂ adsorption on the ZnO surface.^{16,17} To eliminate the influence of the surface state and improve the performance of ZnO UV detectors, various methods have been investigated such as surface passivation by highly intensive UV irradiation,¹⁸ annealing,¹⁹ oxygen plasma treatment,¹⁷ surface modification by other nanomaterials,^{14,20} and so on. Although there is a considerable progress regarding how to reduce or eliminate the influence of the surface state on the performance of ZnO-based UV photodetectors, most of the abovementioned methods are not very effective, and the device performance is still lower than expected.

Previous studies have shown that H₂O₂ solution treatment can efficiently improve the quality of the Schottky contacts between ZnO and electrodes and can also suppress the visible photoluminescence (PL) emission in ZnO associated with oxygen vacancy (V_O) defects.^{21–23} These phenomena indicated that the treatment by H₂O₂ solution can remove the surface V_O and repair the crystal defects of the ZnO film.²⁴ It is thus expected that the performance of ZnO-based photodetectors can be improved *via* the H₂O₂ solution treatment. However, to date, no information can be found about this. In this study, we have investigated the effect of H₂O₂ solution treatment on the performance of a ZnMgO film UV photodetector. It was found that the H₂O₂ solution treatment could dramatically improve the response speed of the ZnMgO UV photodetectors, as well as decrease the dark current of the devices. Moreover, the X-ray diffraction (XRD), energy dispersive spectrometry (EDS), scanning electron

^a State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China. E-mail: liukw@ciomp.ac.cn, shendz@ciomp.ac.cn

^b University of Chinese Academy of Sciences, Beijing 100049, China

microscopy (SEM), and room-temperature photoluminescence (PL) and transmission spectroscopies were utilized to investigate the influence of H_2O_2 solution treatment on the crystalline structure, component, morphology, and optical properties of the ZnMgO films. The mechanism of the property change has been discussed. This result indicates that the solution surface treatment to the device may be an effective way to improve the overall performance of the UV detectors.

Experimental

ZnMgO thin films were grown on a-plane sapphire substrates by plasma-assisted molecular beam epitaxy (P-MBE). 6N-purity zinc and 5N-purity magnesium held in thermal Knudsen cells and 5N-purity O_2 activated in a radio frequency plasma source were selected as precursors. Prior to growth, sapphire substrates were ultrasonically cleaned with a sequence of trichloroethylene, acetone, alcohol and de-ionized water for 10 min in each step, followed by drying with N_2 gas. During the growth of ZnMgO, the substrate temperature was kept at 450°C for 3 hours, and the radio frequency power was fixed at 300 W with O_2 flow rate of 1.0 sccm. In addition, the temperature of Zn and Mg cells were controlled at 215°C and 298°C respectively. Interdigital gold electrodes with a thickness of 30 nm were deposited on the surface of ZnMgO film to fabricate the MSM structured devices by standard photolithography and lift-off technique. The deposition of Au films was carried out at room temperature by sputtering method. Both finger width and gap between fingers were 10 μm , and finger length was 500 μm . After that, the ZnMgO UV detectors were immersed in H_2O_2 solution at 100°C for 3 min. D/max-RA XRD (Rigaku) with Cu K α as the radiation source ($\lambda = 0.154$ nm) was used to investigate the structural properties of ZnMgO. PL (Hitachi F7000) spectra of the samples were measured at room temperature using Xe lamp with a monochromator ($\lambda = 270$ nm) as the excitation source. The current–voltage (I – V) properties and spectral responses were measured using semiconductor parameter analyzer (Keithley 2200) and 200 W UV-enhanced Xe lamp with a monochromator, respectively.

Results and discussion

Fig. 1a shows the XRD patterns of the pristine and H_2O_2 solution-treated ZnMgO films on a-plane sapphire substrates. Besides the (11–20) diffraction peak of the sapphire substrate, only one diffraction peak located at $2\theta = 34.88^\circ$ can be observed, which corresponds to the (0002) orientation of wurtzite ZnMgO.²⁵ After the solution treatment, it was noticed that the (0002) diffraction peak of ZnMgO slightly shifted towards higher-angle side, and the full width at half maximum (FWHM) decreased from 0.20° to 0.18° . The EDS analysis shows an increase in the Zn/Mg ratio of the ZnMgO alloy after H_2O_2 solution treatment, which is presumably associated with a higher hydrolysis rate of MgO than that of ZnO.^{21,23} The effect of H_2O_2 solution treatment on the PL property of the ZnMgO films was investigated,

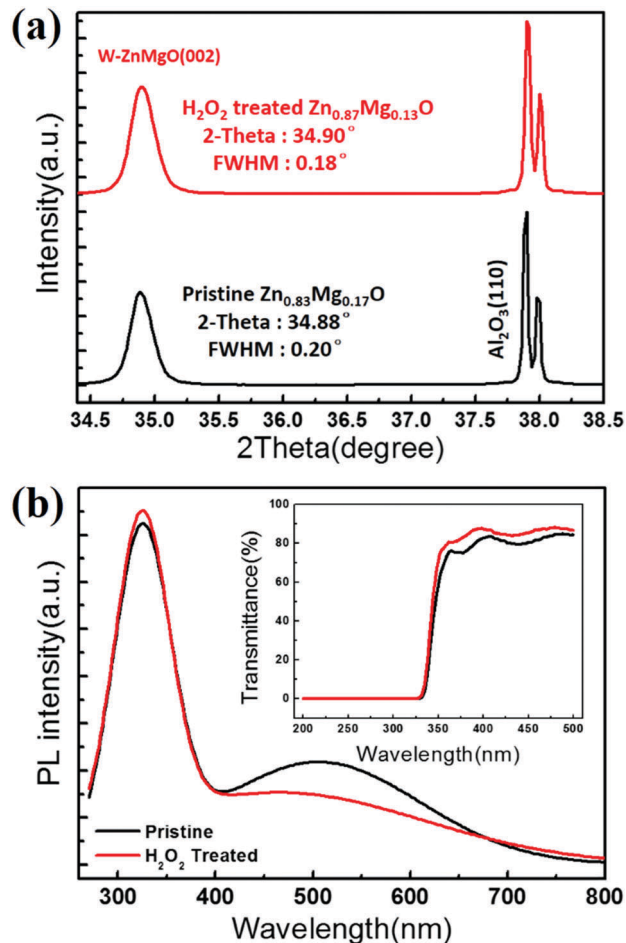


Fig. 1 The XRD pattern (a) and PL spectra (b) of the pristine and H_2O_2 -treated ZnMgO films.

as shown in Fig. 1b. A xenon lamp combined with a monochromator was used as a light source ($\lambda = 270$ nm). The PL spectra of both the pristine and H_2O_2 solution-treated samples exhibit a dominant sharp UV emission peak at 340 nm, which originates from the excitonic recombination corresponding to the band edge emission of ZnMgO.²⁶ In addition, an obvious visible emission associated with V_O defects can be observed from the pristine ZnMgO film.²⁷ Interestingly, the H_2O_2 solution treatment could distinctly suppress the visible emission. It is preferably suggested that most of the oxygen vacancies both on the surface and in the bulk of the ZnMgO film are filled *via* the solution treatment.^{28,29} The transmission spectra (inset of Fig. 1b) indicate that the H_2O_2 solution-treated ZnMgO film has a higher transmittance in the visible region with a sharper edge at about 350 nm in comparison with pristine ZnMgO.

Fig. 2 presents the SEM images of the pristine (Fig. 2a) and H_2O_2 solution-treated (Fig. 2b) ZnMgO films. In Fig. 2a, it is obvious that the pristine ZnMgO film has a rough surface with hexagonal pyramid-shaped nanostructures as well as some nanoparticles. After the treatment *via* H_2O_2 solution, the surface of ZnMgO was composed of a large amount of uniform nano-grains, as shown in Fig. 2b. Additionally, H_2O_2 solution treatment could

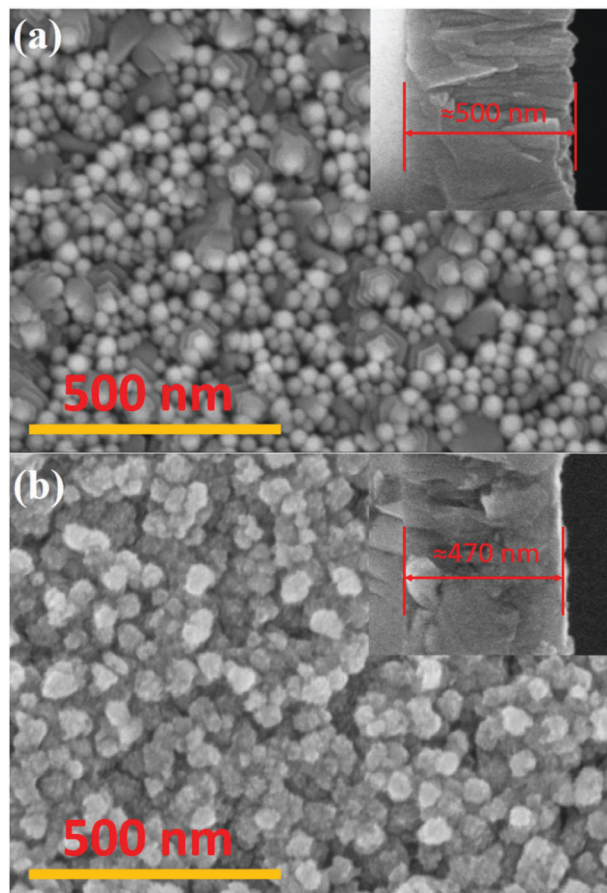


Fig. 2 Top-view and side-view (inset) SEM images of pristine (a) and H_2O_2 treated (b) ZnMgO films.

decrease the thickness of the ZnMgO film from ~ 500 nm to ~ 470 nm (see the insets of Fig. 2a and b). Fig. 3a displays the dark current–voltage (I – V) curves of the ZnMgO detectors with and without H_2O_2 solution treatment. The linear I – V relationship indicates the formation of Ohmic-like contacts between

Au electrodes and ZnMgO films for both devices. After the treatment by H_2O_2 solution, the dark current remarkably decreased by more than one order of magnitude. The spectral response of the pristine and H_2O_2 solution-treated ZnMgO detectors was measured under 1 V bias, as shown in Fig. 3b. It can be seen that the response peak appeared at around 326 nm with a -3 dB cut-off wavelength of 350 nm for both devices, which is in good agreement with the transmission spectra shown in Fig. 1b. After treatment with the H_2O_2 solution, the peak responsivity decreased from 14 A W^{-1} to 4 A W^{-1} . Moreover, the UV/visible rejection ratio ($R_{326 \text{ nm}}/R_{500 \text{ nm}}$) was more than four orders of magnitude for both devices.

To investigate the effect of H_2O_2 solution treatment on the response speed of the ZnMgO photodetectors, time-dependent photoresponse measurement was carried out both in vacuum and oxygen atmosphere by periodically turning on and off the 330 nm light under 1 V bias, as shown in Fig. 4. In vacuum, the current of the pristine ZnMgO photodetector decays very slowly and does not recover to the initial value (Fig. 4a). In contrast, the speed of this device would be obviously increased on exposure to oxygen (Fig. 4b). The slow photocurrent decay and its obvious dependence on atmosphere indicate that the oxygen chemisorption process plays an important role in this pristine ZnMgO photodetector. According to the previous reports, after turning off the light, the photogenerated electrons can still contribute to the device current until they are captured by the surface states of ZnMgO.¹³ The oxygen molecules would adsorb on oxygen deficiencies on the ZnMgO surface, which would capture the photogenerated electrons, and the response speed of pristine ZnMgO photodetector in oxygen atmosphere is thus much quicker than that in vacuum.^{13,16} Interestingly, after treatment with the H_2O_2 solution, the device has the similar rise/decay time both in vacuum and an oxygen atmosphere. This result indicates that H_2O_2 solution treatment can remove the V_O defects on the ZnMgO surface, which is in good agreement with the PL result as shown in Fig. 1b. Thus, the response speed of the solution-treated device is insensitive to the atmosphere.

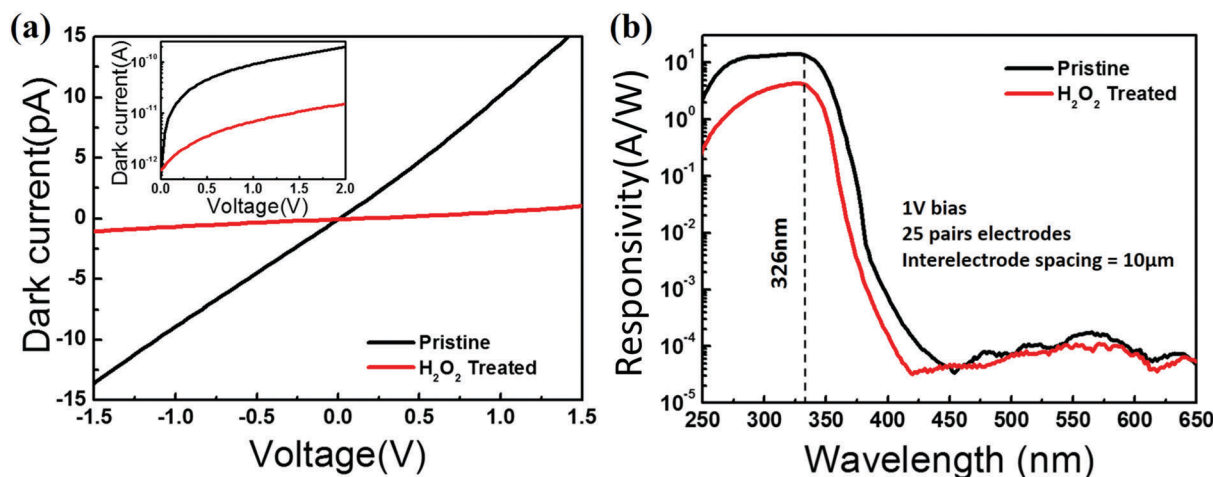


Fig. 3 (a) The dark current–voltage (I – V) curves of the ZnMgO detectors with and without H_2O_2 treatment. (b) The spectral response of the ZnMgO detectors under 1 V applied bias.

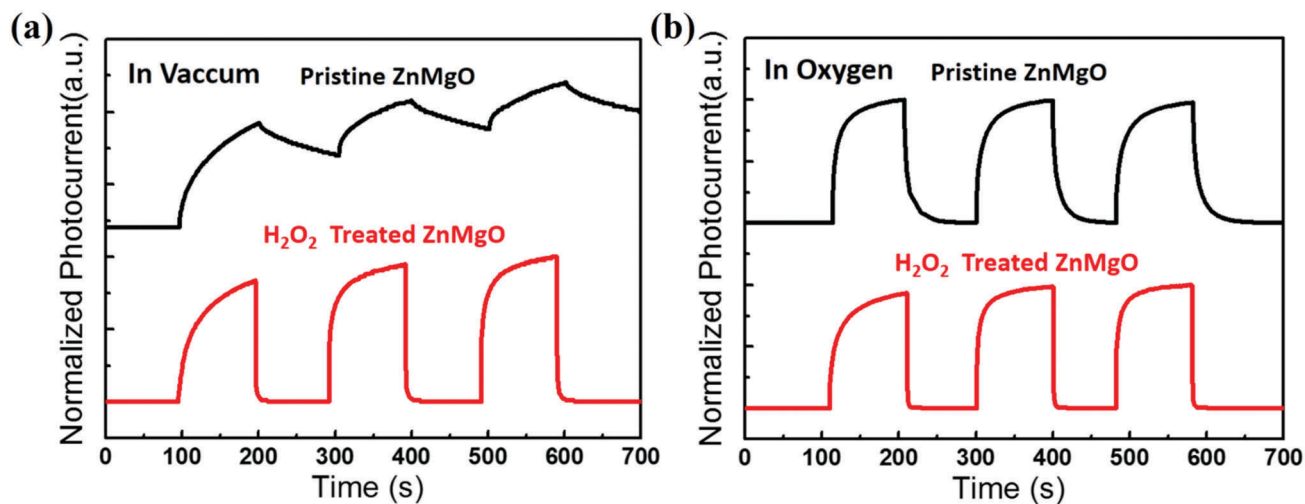


Fig. 4 Temporal response of the detectors measured by shutting on/off the 330 nm light under a 1 V applied bias in vacuum (a) and oxygen (b).

Moreover, compared to the pristine ZnMgO photodetector, H₂O₂ solution-treated device exhibits better on/off switching performance with higher stability and reproducibility. The recovery time (decay time) was extracted from the time taken to reach 10% of the photocurrent after switching off the light. For the pristine ZnMgO photodetector, the recovery time is

more than 10 hours and ~ 4 s in vacuum and in an oxygen atmosphere, respectively. After treatment with the H₂O₂ solution, the recovery time is decreased to less than 1 s both in vacuum and in an oxygen atmosphere.

ZnMgO photodetector treated with H₂O₂ solution shows a lower dark current and a faster response speed as compared to

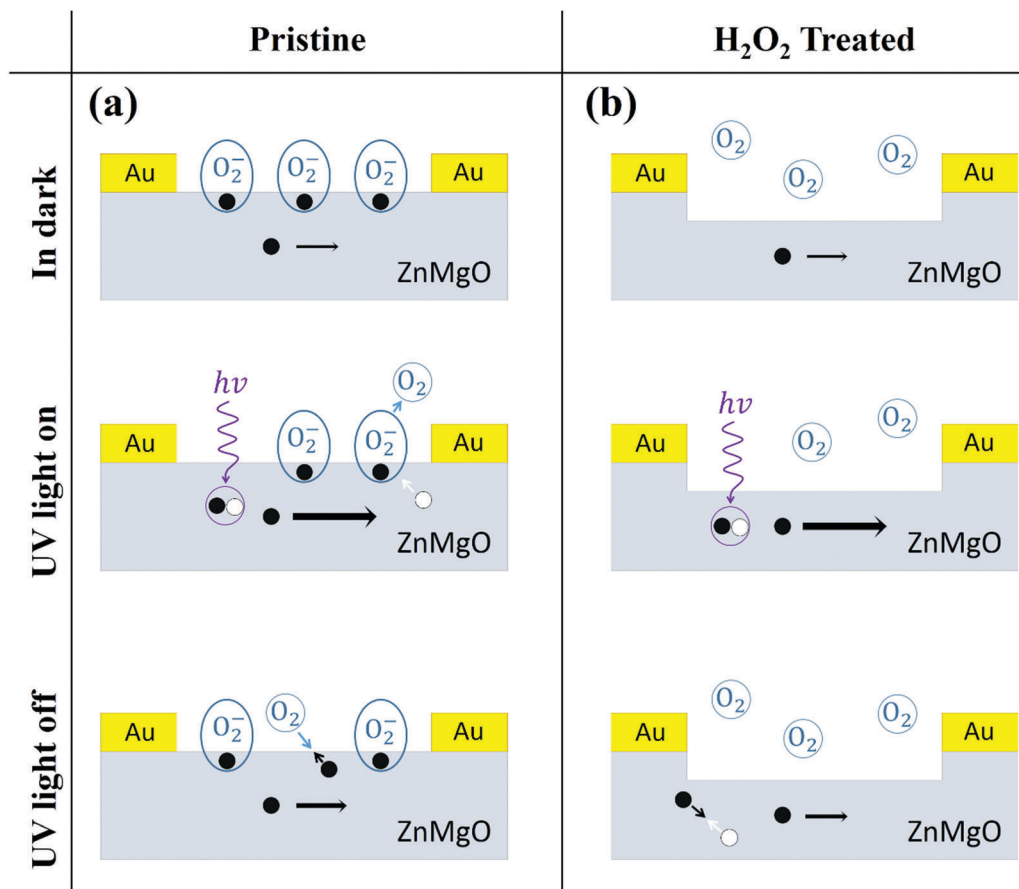


Fig. 5 Schematic of the photoresponse process of pristine (a) and H₂O₂-treated (b) ZnMgO detectors.

the pristine device. To obtain good understanding of the mechanisms of the performance enhancement *via* solution treatment, a model based on the surface effect was proposed, as shown in Fig. 5. For the pristine ZnMgO, there are a large number of V_O defects on its surface. In the dark, oxygen molecules will be adsorbed on these defect states and capture free electrons.¹⁷ After treatment with the H_2O_2 solution, the gas molecules cannot be adsorbed on the surface of the ZnMgO film due to the removal of the surface V_O defects; this would partly increase the dark current. However, the filling of the V_O defects, which usually act as electron donors, in the bulk of ZnMgO could strongly decrease the conductivity of ZnMgO. Additionally, the solution treatment can cause the ZnMgO film thinning, and the corresponding schematic device structure is shown in Fig. 5b. The formation of the ZnMgO neck between Au electrodes and ZnMgO film should also decrease the dark current. Therefore, the dark current of the solution-treated device is much smaller than that of pristine device. Under UV light, photogenerated carriers promote the desorption process of adsorbed oxygen molecules for the pristine ZnMgO photo-detectors. During the desorption process, the trapped electrons are free to conduct. After turning off the light, the readsorption of the gas will reduce the concentration of the photogenerated carriers; thus, the oxygen gas concentration in the environment will affect the lifetime of the photogenerated carriers, as previously mentioned.^{13,15,16} After treatment with the H_2O_2 solution, due to the effective removal of the V_O defects, the gas adsorption effect should be very weak, and thus, the response speed of the device is found to be insensitive to the gas atmospheres.

Conclusions

In summary, ZnMgO thin film UV photodetectors were prepared on a-plane sapphire substrates by plasma-assisted MBE technique, and their performance was investigated before and after treatment with the H_2O_2 solution. After immersing the detector in H_2O_2 solution at 100 °C for 3 min, the dark current of the UV detector is reduced by more than one order of magnitude, and the recovery time can be decreased from more than 10 hours to less than 1 s in vacuum. Additionally, the response speed of the solution-treated device is found to be insensitive to the gas atmosphere. This phenomenon could be explained by the removal of V_O defects due to the H_2O_2 solution treatment, which was confirmed by the PL results. Our findings in this study indicate that the solution surface treatment of the device may be an effective way to improve the overall performance of the UV detectors.

Acknowledgements

This work was supported by the National Natural Science Foundation of China under Grant 61475153, 61605200, 61505200, 61376054, 11374296, the National Science Fund for Distinguished Young Scholars 61425021, 61525404, and the 100 Talents Program of the Chinese Academy of Sciences.

Notes and references

- H. W. Lin, S. Y. Ku, H. C. Su, C. W. Huang, Y. T. Lin, K. T. Wong and C. C. Wu, *Adv. Mater.*, 2005, **17**, 2489–2493.
- Y. N. Hou, Z. X. Mei, Z. L. Liu, T. C. Zhang and X. L. Du, *Appl. Phys. Lett.*, 2011, **98**, 103506.
- D. Gedamu, I. Paulowicz, S. Kaps, O. Lupan, S. Wille, G. Haidarschin, Y. K. Mishra and R. Adelung, *Adv. Mater.*, 2014, **26**, 1541–1550.
- Y. K. Mishra, G. Modi, V. Cretu, V. Postica, O. Lupan, T. Reimer, I. Paulowicz, V. Hrkac, W. Benecke, L. Kienle and R. Adelung, *ACS Appl. Mater. Interfaces*, 2015, **7**, 14303–14316.
- K. W. Liu, M. Sakurai and M. Aono, *Sensors*, 2010, **10**, 8604–8634.
- S. Liang, H. Sheng, Y. Liu, Z. Huo, Y. Lu and H. Shen, *J. Cryst. Growth*, 2001, **225**, 110–113.
- H. Ohta, M. Kamiya, T. Kamiya, M. Hirano and H. Hosono, *Thin Solid Films*, 2003, **445**, 317–321.
- T. K. Lin, S. J. Chang, Y. K. Su, B. R. Huang, M. Fujita and Y. Horikoshi, *J. Cryst. Growth*, 2005, **281**, 513–517.
- Z. Wang, X. Zhan, Y. Wang, S. Muhammad, Y. Huang and J. He, *Nanoscale*, 2012, **4**, 2678–2684.
- C. Lin, S. Chang, W. Chen and T. Hsueh, *RSC Adv.*, 2016, **6**, 11146–11150.
- A. F. Kohan, G. Ceder, D. Morgan and C. G. Van de Walle, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2000, **61**, 15019–15027.
- E. G. Barbagiovanni, V. Strano, G. Franzò and S. Mirabella, *Appl. Phys. Lett.*, 2016, **109**, 143104.
- C. Soci, A. Zhang, B. Xiang, S. A. Dayeh, D. P. R. Aplin, J. Park, X. Y. Bao, Y. H. Lo and D. Wang, *Nano Lett.*, 2007, **7**, 1003–1009.
- K. W. Liu, M. Sakurai, M. Y. Liao and M. Aono, *J. Phys. Chem. C*, 2010, **114**, 19835–19839.
- D. H. Zhang, *Mater. Chem. Phys.*, 1996, **45**, 248–252.
- Q. Chen, H. Ding, Y. Wu, M. Sui, W. Lu, B. Wang, W. Su, Z. Cui and L. Chen, *Nanoscale*, 2013, **5**, 4162–4165.
- B. J. Coppa, R. F. Davis and R. J. Nemanich, *Appl. Phys. Lett.*, 2003, **82**, 400–402.
- D. Zhang, Y. Sheng, J. Wang, F. Gao, S. Yan, J. Wang, L. Pan, Q. Wan and Y. Shi, *Opt. Commun.*, 2017, **395**, 72–75.
- C. Tian, D. Jiang, Z. Tan, Q. Duan, R. Liu, L. Sun, J. Qin, J. Hou, S. Gao, Q. Liang and J. Zhao, *Mater. Res. Bull.*, 2014, **60**, 46–50.
- J. Lu, C. Xu, J. Dai, J. Li, Y. Wang, Y. Lin and P. Li, *Nanoscale*, 2015, **7**, 3396–3403.
- R. Schifano, E. V. Monakhov, B. G. Svensson and S. Diplis, *Appl. Phys. Lett.*, 2009, **94**, 132101.
- Q. L. Gu, C. K. Cheung, C. C. Ling, A. M. C. Ng, A. B. Djurišić, L. W. Lu, X. D. Chen, S. Fung, C. D. Beling and H. C. Ong, *J. Appl. Phys.*, 2008, **103**, 093706.
- Q. L. Gu, C. C. Ling, X. D. Chen, C. K. Cheng, A. M. C. Ng, C. D. Beling, S. Fung, A. B. Djurišić, L. W. Lu, G. Brauer and H. C. Ong, *Appl. Phys. Lett.*, 2007, **90**, 122101.

- 24 H. Y. Lee, C. T. Su, B. K. Wu, W. L. Xu, Y. J. Lin and M. Y. Chern, *Jpn. J. Appl. Phys.*, 2011, **50**, 088004.
- 25 Y. M. Lu, C. X. Wu, Z. P. Wei, Z. Z. Zhang, D. X. Zhao, J. Y. Zhang, Y. C. Liu, D. Z. Shen and X. W. Fan, *J. Cryst. Growth*, 2005, **278**, 299–304.
- 26 S. H. Kim, H. K. Kim and T. Y. Seong, *Appl. Phys. Lett.*, 2005, **86**, 112101.
- 27 O. Lupan, T. Pauporte, B. Viana, I. M. Tiginyanu, V. V. Ursaki and R. Cortes, *ACS Appl. Mater. Interfaces*, 2010, **2**, 2083–2090.
- 28 Y. Chen, F. Jiang, L. Wang, C. Mo, Y. Pu and W. Fang, *J. Cryst. Growth*, 2004, **268**, 71–75.
- 29 A. A. Peyghan, S. P. Laeen, S. A. Aslanzadeh and M. Moradi, *Thin Solid Films*, 2014, **556**, 566–570.