Digest Journal of Nanomaterials and Biostructures Vol. 10, No. 4, October - December 2015, p. 1403 - 1410

EFFECT OF SURFACE MODIFICATION BY A SELF-ASSEMBLED MONOLAYER ON THE INDIUM ZINC OXIDE FILM-BASED ULTRAVIOLET PHOTODETECTOR

S. P. CHANG*, C. H. WEN, H. H. LIN
Institute of Microelectronics & Department of Electrical Engineering, Center for Micro/Nano Science and Technology, Advanced Optoelectronic Technology Center National Cheng Kung University, Tainan 70101, Taiwan

In this paper, indium zinc oxide (IZO) thin films were deposited on a quartz substrate by radio frequency magnetron sputtering. Surface analysis showed that the IZO film deposited under a flow ratio of 10% oxygen has the smoothest surface, and this was determined to the optimum parameter for the fabrication of the metal-semiconductor-metal (MSM) photodetector. In order to improve the response characteristics of the device, 3-aminopropyltrimethoxysilane (APTMS) was deposited onto the IZO film to improve its surface state, which could, in turn, reduce the negative effect of vacancies and suppress the leakage current path for the IZO photodetector. Following APTMS modification, the dark current of the IZO photodetector decreased by nearly an order and the rejection ratio increased from 325 to 728.

(Received October 17, 2015; Accepted December 9, 2015)

Keywords: Indium-Zinc–Oxide, Photodetector, Self-assembled monolayer

1. Introduction

Transparent conductive oxide (TCO) films have been widely used in the field of optoelectronic devices; for example, photodetectors operating in the deep ultraviolet (DUV) region have attached much attention in recent times for their potential applications in flame sensing, chemical/biological agents detection, convert communications, missile plume sensing, and air and water purification [1-5]. However, the most commonly used TCO, zinc oxide (ZnO), is usually polycrystalline in nature and is dependent on the quantity of inherent defects [6,7]. Therefore, a sputtered amorphous In_2O_3-doped zinc capable of forming amorphous phase has been investigated, IZO film in amorphous phase were reported to have the smaller compressive stress and much smoother surface which makes IZO film exhibited high mobility and good transparent properties [8-11].

Although the control of defects in IZO is superior to that in a ZnO film, the dark current is still large (10^{-6} A) because of a very high density of electrons in the active layer under illumination. even without considering the photoinduced electrons and their impact on the device performance of IZO sensors. Therefore, the surface state plays an important role in the control of defects in an

*Corresponding author: changsp@mail.ncku.edu.tw

IZO film. Surface modification, such as passivation by polymethylmethacrylate (PMMA) [12], has been shown as an effective way to eliminate the effect of surface states. However, IZO may easily suffer surface damage from plasma or the chemical solution during processing. We thus propose a simple method that is free from any negative effects for the surface modification of IZO.

3-aminopropyltrimethoxysilane (APTMS) molecules can anchor to the IZO film by self-assembly. APTMS molecules have been recently shown to serve as bio-functional ligands between IZO and metal nanoparticles. Aziz et al. [13] attached gold nanoparticles on an Al-doped IZO substrate by using APTMS as a linker molecule. Zeng et al. [14] have also reported the effects of APTMS molecules on the optical properties of a ZnO nanocolumn-linker-CdSe quantum dots heterostructure. However, till date, there have been no attempts to investigate the effect of surface modification of the IZO film photodetector by APTMS molecules. In this study, the impact of the APTMS self-assembled monolayer (SAM) on the electrical and optical properties of the IZO photosensor is studied through a detailed analysis of synchrotron radiation based photoelectron spectroscopy. The improvement in the device performance of the APTMS-modified IZO film is described in detail below.

2. Experimental

In this research, an IZO film was deposited on a glass substrate that was cleaned by acetone, isopropyl alcohol, and deionized water. The film was deposited by radio frequency sputtering and the target was sputtered to form an 80-nm-thick active layer through a second shadow mask without heating the substrate. The base pressure of the chamber was about 9×10^{-6} Torr. While sputtering, the working pressure was maintained at 10 mTorr and the O_2/ ($Ar+O_2$) flow ratio was varied from 0% to 20%. The power was fixed at 90 W. To fabricate the photodetector, after cleaning the surface of the active layer, a Ni/Au (40/50nm) layer was thermally evaporated onto the IZO films through a shadow mask to serve as the MSM contact electrodes. In order to modify the surface of the film, the sample was immersed in APTMS at room temperature for 4 h. To remove excess APTMS, the modified IZO sample was rinsed thrice with deionized (DI) water. This sample was called the APTMS-modified IZO MSM photodetector. Figure 1 shows a schematic structure of the fabricated APTMS-modified IZO MSM photodetector.

A B1500A semiconductor parameter analyzer was employed to measure the current-voltage characteristics of the proposed IZO MSM photodetector. The photoresponsivity of the fabricated device was also measured using a 250 Watt Xe lamp dispersed by a monochromator as the light source. The monochromatic light, calibrated with a UV-enhanced Si diode and an optical power meter, was modulated by a mechanical chopper and then collimated onto the front-side of the fabricated device using an optical fibre.

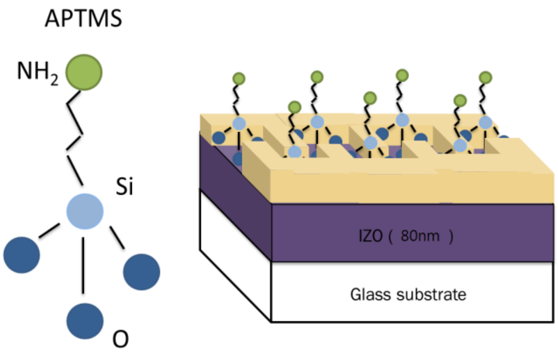


Fig. 1 Schematic of the APTMS-modified IZO film UV sensor.

3. Results and discussion

Fig. 2 (a) (b) shows the XRD patterns of the IZO deposited at various oxygen flow ratios ($O_2/(Ar+O_2)$). The obvious absent of the signal peak from the spectrum, only hump at 21.5° that relative to the glass substrate diffraction signal and the range from 29° –35° without any sharp peak demonstrates that the IZO thin film is under amorphous state. The IZO thin film deposited in an amorphous state could lead to a smooth film surface that can be identified by AFM. The AFM images of the IZO thin film deposited at different oxygen ratios are shown in Fig. 3. The mean roughness of the IZO films are all below 0.5 nm, which is better than the value for a crystallized ZnO thin film [15]. To confirm the atomic composition of the films, the EDS analysis of the IZO thin films at different oxygen flow ratios is shown in Table. 1. It can be found that the oxygen content in the film increases gradually with increasing oxygen flow rate. The transmittance and reflectance of the IZO thin films prior to film modification are shown in Fig. 4(a)-(b). The absorption coefficient spectra of the different thin films are shown in Fig. 5(a)-(b). The value of the band gap was determined from a plot of the square of the absorption coefficient versus photon energy, and the results are shown in Table.2. The result shows that the value of the band gap increases slightly with increasing oxygen ratio. Overall, the band gap was determined to be between 3.73 eV and 3.53 eV.

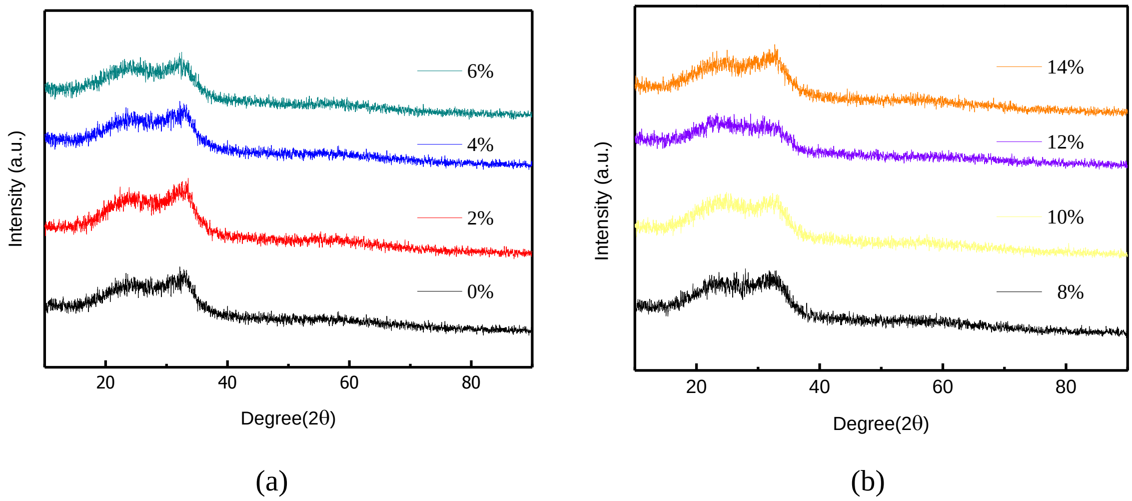


Fig. 2 XRD spectra of the IZO thin film under varying oxygen ratios of (a) 0%-6% and (b) 8%-14%.

Table 1 O_2 composition ratio of the IZO thin film under different oxygen flow ratios.

$O_2/(Ar + O_2)$	0%	2%	4%	6%	8%	10%	12%	14%
$O_2/ (In+Zn+O_2)$	56.11	56.27	59	59.04	57.44	65.18	71	89.35

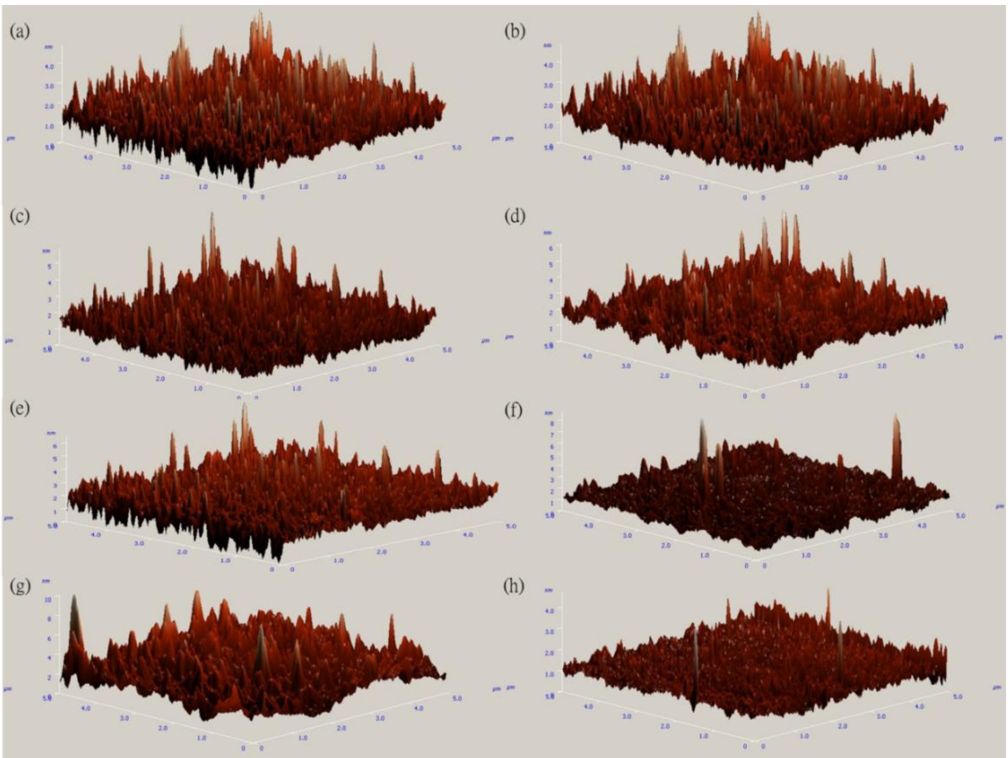
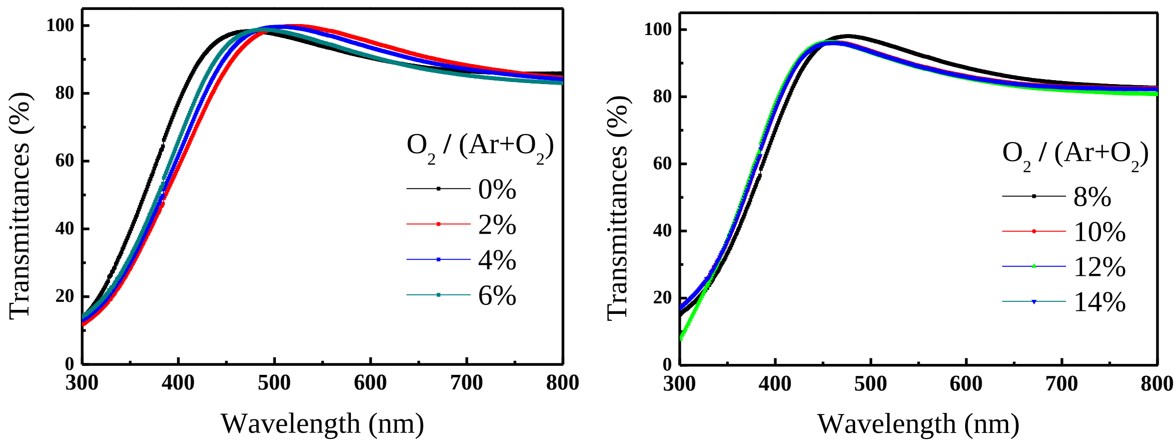


Fig. 3 AFM image of the IZO thin film under varying oxygen ratios of (a) 0%, (b) 2%, (c) 4%, (d) 6%, (e) 8%, (f) 10%, (g)12%, and (h) 14%

Table 2 The band gap and cut-off wavelength of the IZO thin film under different oxygen flow ratios.

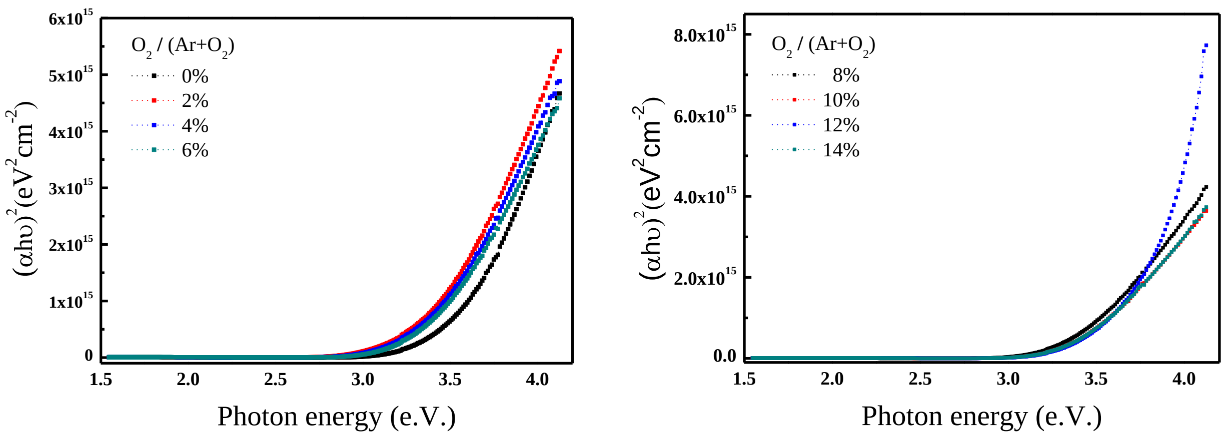
IZO：90W	0%	2%	4%	6%	8%	10%	12%	14%
Eg (eV)	3.53	3.48	3.51	3.50	3.54	3.48	3.73	3.82
Cut-off wavelength(nm)	351	356	353	354	350	356	332	324



(a) (b)

Fig. 4 Transmittance of the IZO thin film under varying oxygen ratios:

(a) 0%-6% and (b) 8%-14%



(a) (b)

Fig. 5 Absorption spectra of the IZO thin film under varying oxygen ratios:

(a) 0%-6% and (b) 8%-14%

In our study, the photodetector deposited under 10% oxygen ratio had the smoothest surface (roughness: 0.4 nm). The characteristics, including the contact angle and responsivity, of the device before and after the film modification are discussed below. From Fig. 8, before modification, the responsivity of the unmodified detector on irradiation with an incident light wavelength of 340 nm and an input bias of 5V was measured to be 2.17A/W. The contact angle (CA) measurements of the IZO film before and after modification with APTMS are shown in Fig. 6; the angle before and after APTMS modification was 88.8° and 65.9°, respectively. Thus, the surface becomes more hydrophilic after the APTMS modification. Therefore, the variation in the contact angle further confirms that the films have indeed been modified. Fig. 7 shows the logarithm output characteristics of the IZO and APTMS-modified IZO MSM photodetector in the dark environment. After the modification with APTMS, the dark current of the photodetector is about an order lower than that of the photodetector without APTMS modification. The surface modification hinders the formation of surface states.

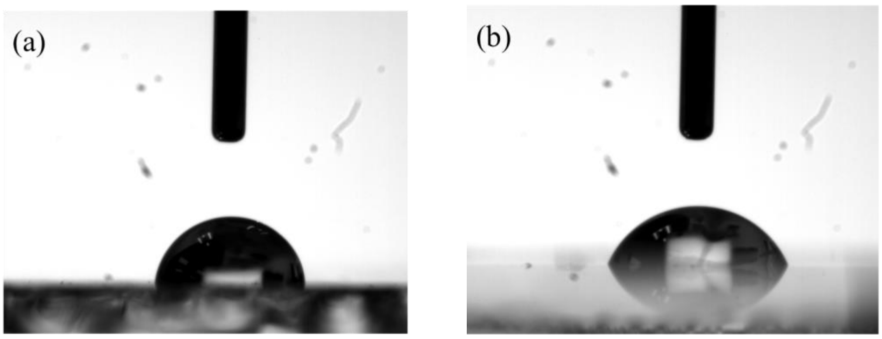


Fig. 6 Contact angle measurements for the (a) IZO film and (b) APTMS-modified IZO film.

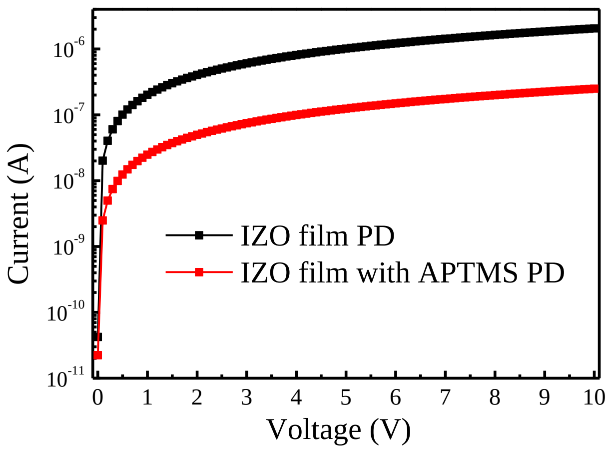


Fig. 7 I-V characteristics of the IZO MSM photodetectors with and without APTMS modification. The measurements were carried out in the dark

As shown in Fig. 8, the spectral responses of the fabricated un-modified and modified photodetector were measured with an applied bias of 5 V. The results show that the cut-off wavelength is around 340 nm, and the responses are flat at short wavelengths, indicating that the devices are indeed visibly blind. The rejection ratio is defined as the responsivity measured at 300 nm divided by the responsivity measured at 450 nm. The measured rejection ratio of IZO and APTMS-modified IZO photodetector are 325 and 728, respectively. This result could be attributed to the fact that the dark current measured from the IZO photodetector was much smaller after modification. From the device perspective, a large dark current would be measured owing to possible Coulomb scattering and/or the presence of a recombination centre. After surface modification by APTMS, the surface states of the IZO film were filled. It indicated that the surface of the film was tightly bonded with siloxane (R-Si-O) molecules and was shown to be of high quality APTMS/IZO interface at which the carrier to flow. Since the IZO surface was passivated by APTMS molecules and oxygen vacancies in the IZO film were compensated, the dark current of the device would be reduced. The difference in the visible light response between the IZO photodetector before and after surface modification is more obvious than the difference in the ultraviolet region. The reason for this difference could be the modification of the IZO film that results in lesser number of surface states. As a result, less energy is absorbed leading to a reduced response in the visible region [16]. Thus, the APTMS-modified IZO photodetector exhibits better characteristics.

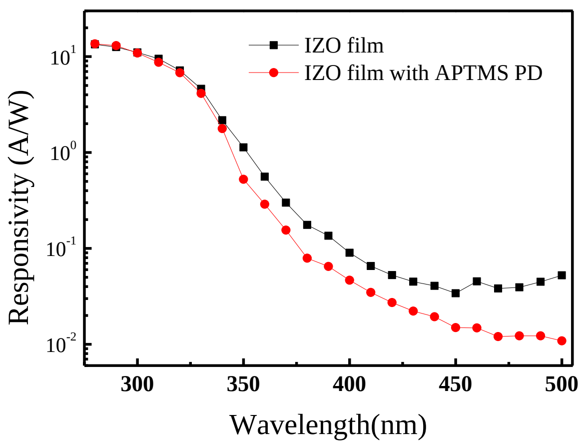


Fig. 8 Photoresponsivity spectra of the IZO MSM photodetectors with and without APTMS modification. The measurements were obtained at an applied bias of 5 V.

4. Conclusions

An IZO thin film was fabricated by sputtering under an oxygen ratio of 10% for an MSM photodetector. The Schottky contact was formed by the Ni/Au electrode. The IZO photodetector has a cut-off wavelength of 340 nm and a responsivity of 2.17 A/W at 340 nm. The rejection ratio is 3.24×10^2. In order to reduce the negative effects of the defects in the IZO film, such as the surface states of the film, we modified the surface of the IZO thin film by a self-assembled monolayer (SAM) of 3-aminopropyltrimethoxysilane (APTMS). Under an applied bias of 5 V, the dark current of the APTMS-modified IZO photodetector is 1.24×10^{-7} and that of the IZO photodetector is 1.01×10^{-6}. The dark current leakage decreases by nearly an order after the APTMS modification, and this leads to a higher contrast in the UV to visible rejection ratio for the APTMS-modified IZO UV photodetector.

Acknowledgment

This work was supported by the Ministry of Science and Technology under contract number MOST 103-2221-E-006-098. This work was also supported in part by the Center for Frontier Materials and Micro/Nano Science and Technology, National Cheng Kung University, Taiwan, and by the Advanced Optoelectronic Technology Center, National Cheng Kung University, under projects from the Ministry of Education.

References

[1] Y. Taniyasu, M. Kasu, T. Makimoto, Nature **441**, 325 (2006).
[2] T. Tut, M. Gokkavas, A. Inal, E. Ozbay, Appl. Phys. Lett. 90, 163506 (2007).
[3] V. Adivarahan, G. Simin, G. Tamulaitis, R. Srinivasan, J. Yang, M. A.Khan, M. S. Shur, R. Gaska, Appl. Phys. Lett. **79**, 1903 (2001).
[4] V. V. Kuryatkov, H. Temkin, J. C. Campbell, R. D. Dupuis, Appl. Phys. Lett. **78**, 3340 (2001).
[5] M. Y. Liao, Y. Koide, J. Alvarez, Appl. Phys. Lett. **90**, 123507 (2007).
[6] H. H. Hsieh, C. C. Wu, Appl. Phys. Lett. **91**, 013502 (2007).
[7] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, H. Hosono, Nature (London) **432**, 488 (2004).
[8] E. Fortunato, P. Barquinha, A. Pimentel, L. Pereira, G. Gonçalves, R. Martins, Phys. Status Solidi-Rapid Res. Lett. **1**, R34 (2007).
[9] H. C. Pan, M. H. Shiao, C. Y. Su, C. N. Hsiao, J. Vac. Sci. Technol. A **23**, 1187 (2005).
[10] R. Martins, P. Barquinha, A. Pimentel, L. Pereira, E. Fortunato, Phys. Status Solidi A-Appl. Mat. **202**, R95 (2005).
[11] T. Sasabayashi, N. Ito, M. Kon, P.K. Song, K. Ustumi, A. Kajio, Y. Shigesato, Thin Solid Films **445**, 219 (2003).
[12] W. K. Hong, B. J. Kim, T. W. Kim, G. Jo, S. Song, S. S. Kwon, A. Yoon, E. A. Stach, T. Lee, Colloid Surf. A-Physicochem. Eng. Asp. **313**, 378 (2008).
[13] M. A. Aziz, M. Oyama, I. V. Kityk, Mater. Lett. **74**, 226 (2012).
[14] T. W. Zeng, I. S. Liu, K. T. Huang, H. C. Liao, C. T. Chien, D. K. P.Wong, C. W. Chen, J. J. Wu, Y. F. Chen, W. F. Su, J. Colloid Interface Sci. **358**, 323 (2011).
[15] J. B. Lee, S. H. Kwak, H. J. Kim, Thin Solid Films **423**, 262 (2003).
[16] T. P. Chen, K.H. Lee, S.P. Chang, S. J. Chang, P. C. Chang, Appl. Phys. Lett. **103**, 022101 (2013)