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Direct ZnO X-Ray Detector with Tunable Sensitivity *

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Direct ZnO x-ray detectors with tunable sensitivity are realized by delicately controlling the oxygen flux during the sputtering deposition process. The photocurrents induced by x-rays from a 40 kV x-ray tube with a Cu anode increase apparently as the oxygen flux decreases, which is attributed to the introduction of V_o detects. By introducing V_o defects, the annihilation rate of the photo-generated electron-hole pairs will be greatly slowed down, leading to a remarkable photoconductive gain. This finding informs a novel way to design the x-ray detectors based on abundant oxide materials.

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X-ray detection has broad applications in medical imaging, cancer treatment, industrial non-destructive testing, public security inspection, x-ray space communication and so on. The energy of x-rays is quite higher than the common photons. For example, medical and space communication x-rays are usually in the range of a few of keV to tens of keV, meaning that they usually have low absorption rate and large penetration depth in most materials, and are quite difficult to detect. Many strategies have been explored to realize the detection of x-rays, including the Geiger–Müller tube, scintillometer, micro-channel plate, charge-coupled devices, silicon drift detectors and so on. Compared with these methods, semiconductor radiation detectors have been developed as a mainstream of x-ray detectors due to their high sensitivity, high signal/noise ratio, high energy resolution and high integration capability. So far, most of the commercialized semiconductor x-ray detectors are based on Si,[1] Se,[2] and CdZnTe.[3] However, a wide range of new materials—such as iodide and perovskite compounds,[4,5] and organic materials,[6]—are being exploited to further improve the x-ray detection performance. However, these new materials are still challenging, considering their stability and repeatability under harsh radiation environment.

Wide band gap semiconductors, owning to their natural radiation hardness and low leakage current, have become another recent trend for x-ray detection. Great efforts have been devoted to investigate the performance of x-ray detectors using wide band gap materials, such as GaN,[7] SiC,[8] diamond,[9] β-Ga_2O_3 and amorphous Ga_2O_3 (a-Ga_2O_3),[10,11] and ZnO.[12–15] Among these materials, ZnO is very attractive due to its low temperature growth, easy crystallization and multi-functionality. Many groups have shown the potential of high resistant ZnO bulk crystals,[12,13] ZnO thin films[14,15] and ZnO nanowires[15] to work as an effective x-ray sensor. However, to the best of our knowledge, there are very few reports regarding the further improvement of the sensitivity of these devices by optimizing their material properties.

In this work, we present x-ray detectors with tunable sensitivity using polycrystalline ZnO thin films deposited by radio frequency (rf) magnetron sputtering technique. Oxygen flux was delicately controlled during the sputtering process. Metal/semiconductor/metal (MSM) structured photodetectors with co-planar interdigital electrodes were fabricated. Irradiated by x-rays from an x-ray tube with a Cu anode biased at 40 kV, the current of the devices increased apparently as the oxygen partial pressure decreases, indicating a large photoconductive gain at the expense of a large response time. It should be noted that even though the thickness of ZnO films in our work is only 300 nm, while those in previous reports are at least 1 μm, the photocurrent of Z2 sample is still very competitive compared with recent result in Ref. [14]. This finding demonstrates that the sensitivity of ZnO x-ray detectors can be effectively tuned with a delicate control of the oxygen flux, establishing a technical foundation for further boost of radiation detectors using ZnO related materials.

ZnO thin films with a thickness of 300 nm were deposited on quartz substrates under different oxygen partial pressures (Z1: 1.0×10^{-3} Pa, Z2: 7.0×10^{-4} Pa, Z3: 0) by rf magnetron sputtering system at room temperature. Our ZnO ceramic target is 4 N pure. The quartz substrates were ultra-sonically cleaned in acetone, alcohol and deionized water successively and blown dry by nitrogen gas before loading into the vacuum chamber with a base pressure of 3.0×10^{-4} Pa. Then, a high purity oxygen gas (5 N) was introduced into the sputtering chamber through a leakage valve,

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the amount of which was monitored by an ion gauge. After the chamber pressure was stabilized, the sputtering gas, argon (Ar), entered into the chamber through a mass flow controller (MFC) maintained at 10.0 sccm. The whole growth process lasted for 30 min with a sputtering power of 60 W and a total pressure of 0.4 Pa. The crystal structure of these ZnO thin films was investigated by x-ray diffraction (XRD) technique. MSM structured photodetectors with coplanar interdigital electrodes were fabricated on these thin films by conventional UV-lithography and lift-off technology. The prototype device has 75 pairs of fingers with 5 μm in width, 5 μm in spacing gap and 300 μm in length. The 100 nm indium tin oxide (ITO) was used as interdigital electrodes. The current-voltage (I–V) tests were carried out in dark and illuminated by UV light and x-ray, respectively, using a picoammeter (Keithley 6487). A hand-held lamp with a 365 nm output was applied as the UV light source. The x-ray source was an x-ray tube with a Cu anode in an x-ray diffraction setup (Smartlab, Rigaku), working at 40 kV and 200 mA.

Figure 1 shows the XRD θ–2θ scans of all of the samples. Six peaks can be clearly distinguished. They are attributed to the diffraction from wurtzite ZnO phase with different crystal planes, as labeled in the picture, indicating that all of the samples are polycrystalline no matter what the oxygen partial pressure is applied during the deposition process.

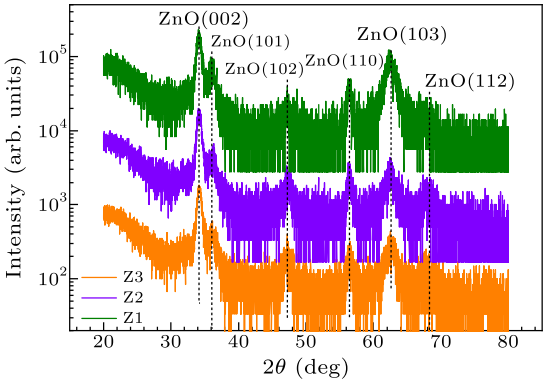

Fig. 1. XRD θ–2θ scans of all the samples. Note that the diffraction intensity is rescaled just for clarity.

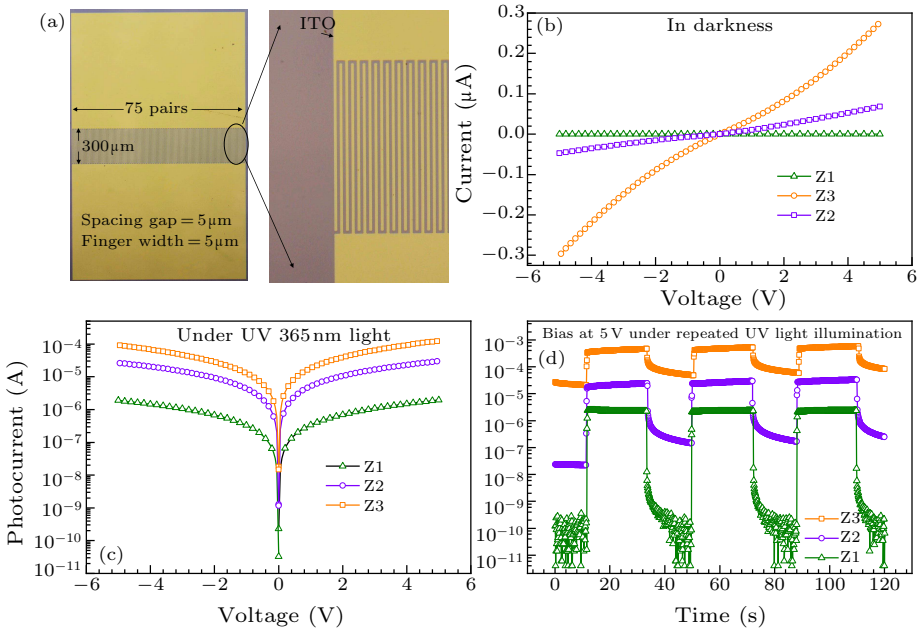

Fig. 2. (a) Microscope photograph of the MSM structured ZnO photodetector on the quartz substrate, (b) I–V curves in darkness, (c) I–V curves under UV 365 nm light illumination, and (d) time-dependent photoresponse of all the devices with the UV 365 nm light on and off at 5 V bias.

The MSM structured photodetectors were fabricated on the ZnO thin films. Fig. 2(a) shows the microscope photograph of the prototype device. Figure 2(b) presents the I–V characteristics of the devices in dark. It can be found that the dark current increases gradually as the oxygen partial pressure decreases from Z1 to Z3. As reported before, V_o defects, which are responsible for the unintentional n-type conductivity, have been widely observed in oxide semiconductor materials, such as ZnO,[16] and In_2O_3.[17] Thus, as the oxygen partial pressure decreases, more V_o defects will be produced in the film, resulting in more carrier concentration and larger dark current. Figure 2(c) shows the I–V curve under 365 nm UV light illumination. The photocurrent decreases about two orders of magnitude as oxygen partial pressure increases from 0 (Z3) to 1.0×10^{-3} Pa (Z1). It has been reported that the decreased n-type doping at the surface will promote the formation of the Schottky contact on the expense of Ohmic behavior.[18] This contact type conversion from Ohmic to Schottky has also been observed by Zhang *et al.* at Ti/a-Ga_2O_3 interface by tuning the conductivity of a-Ga_2O_3 thin films with a delicate control of the oxygen flux dur-

ing deposition process.[19] Therefore, the decrease of the photocurrent can be ascribed to the formation of Schottky contact at ITO/ZnO interface. Figure 2(d) gives the time-dependent UV response of these devices, which demonstrates good repeatability to the periodical UV light illumination. It should be noted the recovery time (90% to 10%) increases from less than 0.11 s of Z1 to more than 15 s of Z3 accompanied by a large photocurrent increase, which is regarded as a consequence of V_o defects.[20]

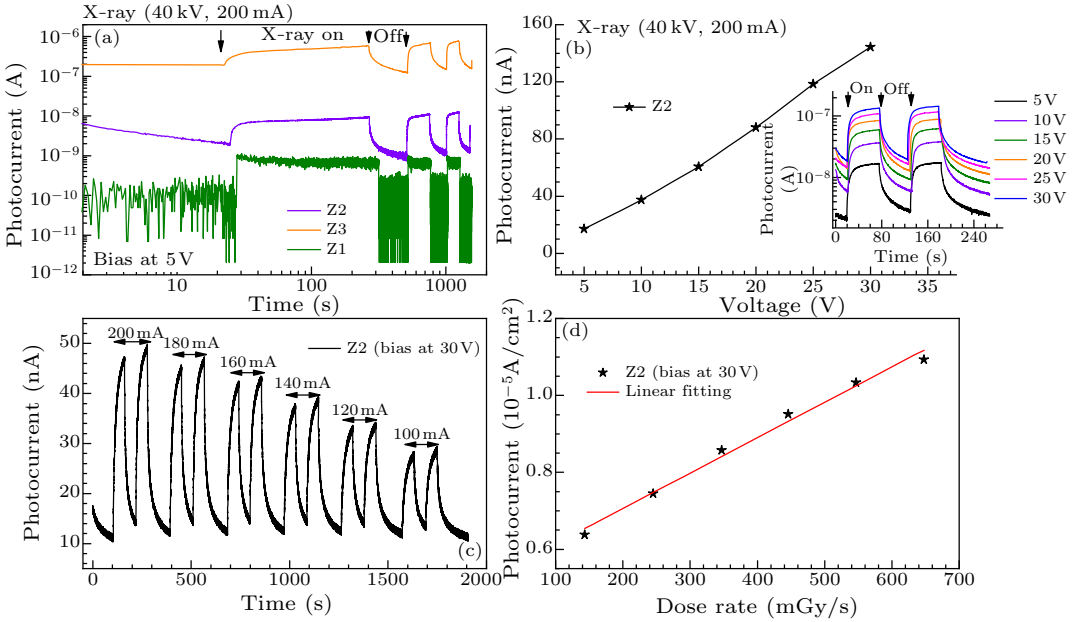

Fig. 3. (a) Time-dependent photocurrent of Z1–Z3 with x-ray source on and off at 5 V bias. (b) Photocurrent of Z2 as a function of the applied bias. The photocurrent value is taken from the 2nd cycle before x-ray is off. (c) Time-dependent photocurrent of Z2 with a 60 s-long x-ray illumination at 30 V bias. (d) X-ray-generated photocurrent at various dose rates.

We then measured their responses to x-ray illumination in air. Figure 3(a) shows the temporary response with x-rays on and off (controlled by an electromechanical shutter) for three cycles at 5 V bias. Similarly, as the UV response shown in Fig. 2(d), all devices demonstrate good repeatability. Importantly, the x-ray induced current also increases more than two orders of magnitude as V_o concentration increases from Z1 to Z3. Dependence of the photocurrent on the applied bias is demonstrated in Fig. 3(b). The measurement was proceeded with the maximum x-ray tube current. It can be observed that the photocurrent increases almost linearly with bias. In Fig. 3(c), we measured the photocurrent of Z2 under a monochromatic x-ray beam to evaluate its sensitivity. Since the intensity of the x-ray beam decreases a lot after monochromatization, the photocurrent also decreases from 144 nA to 44 nA when biased at 30 V with a tube current of 200 mA. Figure 3(d) exhibits the photocurrent at different dose rates. The photocurrent value is taken from the 2nd cycle before x-ray is off in Fig. 3(c). The detailed calculation of the dose rate at corresponding tube current can be found in the supporting information in Ref. [11]. From the linear fit of the experimental data, the slope of the line (i.e., the device sensitivity) is determined to be $9.19\times10^{-3}\,\mu\mathrm{CmGy}_{\mathrm{air}}^{-1}\mathrm{cm}^{-2}$. Considering the ~300 nm thickness of the ZnO active layer, the normalized sensitivity with volume is $306\,\mu\mathrm{CmGy}_{\mathrm{air}}^{-1}\mathrm{cm}^{-3}$, which is slightly higher than the sensitivity of our previously reported a-Ga_2O_3 x-ray detector.

Table 1. A summary of the rf-sputtered ZnO x-ray detectors performance. The dark current and photocurrent values are taken from the 1st cycle before x-ray is on and off, respectively.

Sample	Oxygen partial pressure (Pa)	Dark current@5 V (A)	X-ray photocurrent@5 V (A)	Recovery time(80%–20%) (s)
Z1	1.0×10^{-3}	1.5×10^{-10}	7.0×10^{-10}	≤ 0.11
Z2	7.0×10^{-4}	2.0×10^{-9}	1.2×10^{-8}	43
Z3	0	2.8×10^{-7}	7.7×10^{-7}	285

Table 1 lists all the performance parameters of the three devices, from which it can be clearly seen that both the dark current and x-ray photocurrent increase with a decreased oxygen partial pressure. More importantly, the recovery time also increases greatly from less than 0.11 s of Z1 to 285 s of Z3, demonstrating a typical persistent photoconductivity (PPC) effect. It is widely accepted that inherent PPC effect in oxide materials is related to V_o defects.[20] By introducing V_o defects, both the conductivity of the film and the Ohmic contact of the ITO/ZnO interface will be improved, which is beneficial for the enhancement of the

dark current and photocurrent. However, it is unfavorable to realize a high signal/noise ratio at the expense of an increased dark current, which should be considered in future investigations. Moreover, it should be noted that the thickness of the ZnO film is only about 300 nm, meaning that only ∼1‰ x-ray photons can be absorbed by such a thin active layer. Nevertheless, the Z2 device behaves as a decent x-ray detector. It may originate from the speculation that when illuminated by x-rays, energetic electrons will be produced and can impact atoms around them to transfer their excessive energy by creating new e-h pairs, which is like the cascade effect. In addition, the ionized V_o defects will suppress the recombination of the electrons and holes once they are excited by incident x-ray photons,[21] greatly slowing down the annihilation rate and leading to a remarkable photoconductive gain. All of these factors can compensate for the drawback of low absorption of x-rays in ZnO thin films. This observation is consistent with our previous work using a-Ga_2O_3 as an active layer for x-ray detection.[11]

Table 2. Comparison with the sensitivity of the various detectors presented in the references.

Material	Thickness (μm)	Voltage (V)	Dark current	Photocurrent	X-ray dose rate	Sensitivity in the reference
PbI_2[4]	500	50	30 pA	∼10 nA	140 R/min	45 nC·mm^{-2}R^{-1}
$CH_3NH_3PbI_3$[5]	830	50	80 nA/cm^2	∼5×10^{-3} mA/cm^2	1 mGy/s	11 μC·mGy$_{air}^{-1}$cm^{-2}
Polymer(PFO)[6]	20	50	0.9 nA	4.5 nA	18.5 mGy/s	480 nC·mGy^{-1}cm^{-3}
β-Ga_2O_3[10]	1000	−15	∼1 μA/cm^2	∼1×10^{-3} A/cm^2	4.596 Gy/s	
a-Ga_2O_3[11]	0.25	50	∼0.2 nA	∼15 nA	650 mGy/s	271 μC·mGy$_{air}^{-1}$cm^{-3}
ZnO bulk[12]	500	50	∼25 pA	∼30 nA	1.53 Gy/s	19.4 nC/Gy
ZnO bulk[13]	500	20	∼50 pA	∼275 pA	307 μGy/s	1.5 μC/Gy
ZnO film[14]	3	40	∼0.1 nA	∼30 nA	1.532 Gy/s	25 nC/Gy
ZnO film[15]	1.4	100	∼0.1 mA	∼1.0 mA	10 mC/(kg·s)	0.12 μC/Gy
ZnO NWs[15]	1	50	∼1.5 mA	∼3.0 mA	10 mC/(kg·s)	0.17 μC/Gy
ZnO (Z2)[Thiswork]	0.3	30	∼10 nA	44 nA	650 mGy/s	306 μC·mGy$_{air}^{-1}$cm^{-3}

Finally, we further compared the sensitivity value of our device with various detectors presented in the references as listed in Table 2. From this comparison, it can be clearly found that both the dark current and sensitivity of the Z2 device are competitive to all of the other devices.

In summary, we have presented rf-sputtered ZnO based x-ray detectors with tunable sensitivity. The x-ray induced photocurrent can be increased by more than two orders of magnitude as oxygen partial pressure decreases from 1.0×10^{-3} Pa to 0 Pa. The enhancement of the photocurrent is ascribed to the fact that the annihilation rate of the photon-generated carriers will be slowed down due to the introduction of V_o defects, indicating a large photoconductive gain at the expense of a long response time. This work reveals an easy method to tune the sensitivity of the x-ray detector based on oxide materials, opening a new avenue to design novel x-ray detection system.

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References

[1] Guazzoni C 2010 *Nucl. Instrum. Methods Phys. Res. Sect. A* **624** 247
[2] Kasap S, Frey J B, Belev G, Tousignant O, Mani H, Laperriere L, Reznik A and Rowlands J A 2009 *Phys. Status Solidi B* **246** 1794
[3] Sordo S D, Abbene L, Caroli E, Mancini A M, Zappettini A and Ubertini P 2009 *Sensors* **9** 3491
[4] Sun H, Zhu X H, Yang D Y, Wangyang P H, Tian H B and Gao X Y 2016 *IEEE Trans. Nucl. Sci.* **63** 1790
[5] Kim Y C, Kim K H, Son D Y, Jeong D N, Seo J Y, Choi Y S, Han I T, Lee S Y and Park N G 2017 *Nature* **550** 87
[6] Boroum, F A, Zhu M, Dalton A B, Keddie J L, Sellin P J and Gutierrez J J 2007 *Appl. Phys. Lett.* **91** 033509
[7] Duboz J Y, Frayssinet E, Chenot S, Reverchon J L and Idir M 2010 *Appl. Phys. Lett.* **97** 163504
[8] Nava F, Bertuccio G, Cavallini A and Vittone E 2008 *E Meas. Sci. Technol.* **19** 102001
[9] Conte G, Rossi M C, Salvatori S, Ascarelli P and Trucchi D 2004 *J. Appl. Phys.* **96** 6415
[10] Lu X, Zhou L D, Chen L, Ouyang X P, Liu B, Xu J and Tang H L 2018 *Appl. Phys. Lett.* **112** 103502
[11] Liang H L, Cui S J, Su R, Guan P F, He Y H, Yang L H, Chen L M, Zhang Y H, Mei Z X and Du X L 2019 *ACS Photon.* **6** 351
[12] Zhao X L, Chen L, He Y N, Liu J L, Peng W B, Huang Z Y, Qi X M, Pan Z J, Zhang W T, Zhang Z B and Ouyang X P 2016 *Appl. Phys. Lett.* **108** 171103
[13] Endo H, Chiba T, Meguro K, Takahashi K, Fujisawa M, Sugimura S, Narita S, Kashiwaba Y and Sato E 2011 *Nucl. Instrum. Methods Phys. Res. Sect. A* **665** 15
[14] Zhou L D, Huang Z Y, Zhao X L, He Y N, Chen L, Xu M X, Zhao K, Zhang S C and Ouyang X P 2019 *IEEE Photon. Technol. Lett.* **31** 365
[15] Zhao X L, Kang X, Chen L, Zhang Z B, Liu J L, Ouyang X P, Peng W B, He Y N 2014 *Acta Phys. Sin.* **63** 098502 (in Chinese)
[16] Liu L S, Mei Z X, Tang A H, Azarov A, Kuznetsov A, Xue Q K and Du X L 2016 *Phys. Rev. B* **93** 235305
[17] Tang A H, Mei Z X, Huo W X and Du X L 2018 *Sci. Chin.-Phys. Mech. Astron.* **61** 117321
[18] Monakhov E V, Kuznetsov A Y and Svensson B G 2009 *J. Phys. D* **42** 153001
[19] Zhang Y F, Chen X H, Xu Y, Ren F F, Gu S L, Zhang R, Zheng Y D and Ye J D 2019 *Chin. Phys. B* **28** 028501
[20] Lany S and Zunger A 2005 *Phys. Rev. B* **72** 035215
[21] Hu W J, Paudel T R, Lopatin S, Wang Z, Ma H, Wu K, Bera A, Yuan G, Gruverman A, Tsymbal E Y and Wu T 2018 *Adv. Funct. Mater.* **28** 1704337