# ZnON Thin Film and Its Impact on the IGZO Phototransistor

## Yuseong Jang<sup>1</sup>, Kyeong Soo Kang<sup>1</sup>, Soo-Yeon Lee<sup>1</sup>

sooyeon.lee@snu.ac.kr

<sup>1</sup>Department of Electrical and Computer Engineering and Inter-university of Semiconductor Research Center, Seoul National University, Seoul 08826, Republic of Korea

Keywords: ZnON, metal oxynitride, reactive sputtering, InGaZnO (IGZO), phototransistor

## ABSTRACT

We fabricated IGZO/ZnON phototransistor by adopting in-situ deposition of IGZO and ZnON thin films. ZnON thin film, deposited using ZnO ceramic target, successfully enhanced the recombination of  $V_0^{2+}$  states in IGZO so that negligible persistent photoconductivity (PPC) effect was achieved.

#### 1 Introduction

Over the past years, IGZO has been utilized for various optoelectronic devices such as neuromorphic computing and photodetector [1, 2]. It is attributed to promising characteristics of IGZO, which involve low-temperature process and moderate electron mobility. Besides, IGZO exhibits transparency and detects UV photons owing to a wide optical bandgap (>3.0 eV). In fact, IGZO can absorb photons in the visible range by photo-excitation of oxygen vacancy (V<sub>0</sub>) to form V<sub>0</sub><sup>2+</sup> and 2e<sup>-</sup>. However, a severe drain current is usually observed in IGZO TFT after the light-off, which is called PPC effect. This PPC effect prohibits IGZO TFT from distinguishing light illumination conditions and deteriorates the dynamic range as a photodetector. In other words, the PPC effect should be minimized, which can be realized by the passivation of Vo, the main origin of PPC effect.

ZnON has been employed as an alternative because nitrogen with a higher 2p orbital energy than oxygen can occupy V<sub>0</sub> states that are widely distributed above the valence band maximum (VBM) of ZnO-based materials [3]. In addition, the optical bandgap can be narrowed with nitrogen incorporation due to VBM upshift induced by repulsion between *p* orbital of anions and *d* orbital of Zn.

The general method to prepare ZnON was a reactive sputtering using metallic Zn target under the gas mixtures of Ar,  $O_2$ , and  $N_2$  [4, 5]. Most studies mainly focused on N-rich ZnON; however, it has been recently reported that optoelectronic properties were degraded by excess nitrogen [6, 7]. Thus, intermediate nitrogen incorporation is desired.

In this study, ZnON thin film was prepared by radiofrequency (RF) magnetron sputtering using ZnO ceramic target. There have been some literatures where ZnO ceramic target was used for ZnON thin film, and TFT by reactive sputtering [8] and pulsed laser deposition (PLD) [9, 10], respectively. To our knowledge, this is the early report on ZnON TFTs utilizing ZnO ceramic target. Optical, structural, and chemical properties of ZnON thin film were characterized. The device performance of ZnON TFT was compared with those of ZnO and IGZO TFT. Finally, IGZO/ZnON phototransistor was demonstrated with negligible PPC effect and improved photo-response.

#### 2 Experiment

Three kinds of thin film (ZnO, ZnON, and IGZO) were prepared by RF magnetron sputtering at room temperature using ZnO (purity:99.999 %) and IGZO (purity:99.99 %; In:Ga:Zn=1:1:1 at%) ceramic targets. The base pressure was evacuated below  $5x10^{-7}$  Torr by turbomolecular pump. ZnO was deposited under the Ar/O<sub>2</sub> mixture with each of gas flow rate at 20/1 sccm. ZnON was prepared under the pure nitrogen plasma where the flow rate of N<sub>2</sub> was 100 sccm. The RF power for ZnO and ZnON was 70 W. IGZO was grown under the Ar/O<sub>2</sub> mixture with each of gas flow rate at 50/0.5 sccm at a RF power of 90 W. The purity of all gases was 99.999 %. The thickness and working pressure for single channels were fixed at 30 nm and 5 mTorr.

Fig. 1 shows the schematic of device structure and TFT fabrication sequence. Heavily doped p-type silicon substrate with thermally grown SiO<sub>2</sub> (200 nm) was used as a gate and gate dielectric, respectively. The substrate was cleaned by sonication in acetone, ethanol, and DI water for 10 min each and then dried by N<sub>2</sub> blowing. The semiconductors were deposited above the SiO<sub>2</sub>. For IGZO/ZnON phototransistor, pre-sputtering of ZnO target under pure Ar plasma for 10 min was performed after IGZO deposition and prior to ZnON deposition. The thickness of IGZO and ZnON was 10 and 20 nm. 120 nm thick AI was thermally evaporated for source and drain electrodes. Finally, TFTs were post annealed in air for 1 hr at 250 °C. All patterns were defined by metal shadow masks and the channel length and width were 90 and 1000 µm.



Fig. 1 Device structure and fabrication sequence

The absorption spectra of thin films were obtained by UV-visible spectrophotometer (UV-Vis, Hitachi, U-2900). The optical bandgap was determined by Tauc plot. Top view image of ZnON was characterized by scanning electron microscope (SEM, ZEISS, Merlin Compact). The atomic compositions were analyzed through energy dispersive spectroscopy (EDS) equipped on SEM under 8.0 x 10<sup>-7</sup> Torr to improve accuracy. For SEM and EDS analysis, ZnON thin film on silicon substrate was used after HF etching to eliminate the native oxide. The crystal structure was identified by grazing incidence X-ray diffraction (GIXRD, PANalytical, X'pert Pro) utilizing Cu Ka radiation. The chemical states were studied by X-ray photoelectron spectroscopy (XPS; PHI, Versaprobe III) after Ar<sup>+</sup> ion sputtering (2 kV) for 100 s. The electrical properties of TFT were measured using a Keithely 4200-SCS semiconductor parameter analyzer under ambient conditions. To evaluate the phototransistor performance, blue light ( $\lambda$ =450 nm, intensity= 7 mW/cm<sup>2</sup>) was used.

### 3 Results

Fig. 2 shows Tauc plots of ZnO and ZnON. The optical bandgap was determined to be 3.26 and 1.84 eV, respectively. The inset in Fig. 2 shows digital photograph of ZnON thin film deposited on the glass substrate with brownish color. This reflects that substantial nitrogen incorporation is also possible by reactive sputtering of ZnO ceramic target under nitrogen plasma.

Fig. 3 shows GIXRD spectra of ZnO and ZnON to investigate the structural property. ZnO thin film had the highest intensity of (002) diffraction pattern which corresponds to hexagonal (wurtzite) structure. In contrast, three weak diffraction patterns of cubic  $Zn_3N_2$  were observed in ZnON thin film with broad distributions in the range from 30° to 40°. This indicates a highly disordered structure due to substitution of nitrogen with oxygen within the fundamental ZnO matrix. This agrees well with the previous studies where ZnON deposited by reactive sputtering of metallic Zn target exhibited amorphous/nanocrystalline mixed phase [11]. We therefore believe that our ZnON thin film is mixed phase of amorphous and  $Zn_3N_2$  nanocrystallites.

Fig. 4 shows the surface morphology of ZnON thin film characterized by SEM, implying nanocrystallites formation. The quantitative analysis through EDS mapping revealed that the relative composition was Zn:O:N=48:39:13 at%.

Fig. 5 (a) shows normalized O 1s core level spectra of ZnO and ZnON, indicating that nitrogen has passivated oxygen deficient states in the vicinity of 531 eV. Fig. 5 (b) shows normalized Zn LMM auger spectra, where the entire spectra of ZnON was blue shifted relative to those of ZnO, which was consistent with the previous report [11]. Fig. 5 (c) shows N 1s core level spectra of ZnON composed of non-stoichiometric  $Zn_xN_y$ , stoichiometric  $Zn_3N_2$ , N-N, and NO<sub>2</sub> chemical states. The nitrogen of ZnON thin film mainly participates in forming

stoichiometric Zn<sub>3</sub>N<sub>2</sub> chemical states.



**Fig. 2** Tauc plots of ZnO and ZnON. The inset shows the digital photograph of ZnON thin film.



Fig. 3 GIXRD spectra of substrate, ZnO, and ZnON thin film.



Fig. 4 Top view SEM image and EDS mapping results of ZnON thin film.



Fig. 5 XPS spectra of (a) O 1s, (b) Zn LMM auger, and (c) N 1s.

Fig. 6 (a) shows transfer curves with extracted electrical parameters ( $\mu$ ; mobility, S.S; subthreshold swing, and V<sub>TH</sub>; threshold voltage) of TFTs. Compared with ZnO TFT, the µ and S.S of ZnON TFT were significantly enhanced as a result of nitrogen incorporation. It is attributed to the density functional theory (DFT) calculations that the effective mass of Zn<sub>3</sub>N<sub>2</sub> is smaller than IGZO and In<sub>2</sub>O<sub>3</sub> [3, 13]. Note that for our ZnON thin film, the diffraction patterns and chemical states of Zn<sub>3</sub>N<sub>2</sub> were identified in Fig. 3 and Fig. 5, respectively. Fig. 6 (b) shows the phototransistor performance when blue light was illuminated for 45 s. For ZnO and IGZO TFT, the photocurrent (Ip) consistently increased along the illumination time at higher slope than ZnON TFT. Since the energy of incident blue photon (~2.8 eV) was smaller than the optical bandgap of ZnO and IGZO, the photogeneration by Vo-to-band would be dominant and keep



**Fig. 6** The (a) transfer curves and (b) phototransistor performance under the blue light illumination.

Table 1. The device performance parameters

	ZnO	ZnON	IGZO	IGZO/ZnON
μ (cm²V <sup>-1</sup> s <sup>-1</sup> )	1.06	6	12.73	11.56
S.S (V/dec)	1.79	0.47	0.13	0.37
V <sub>TH</sub> (V)	-5.03	0.3	0.2	2.91
SNR (Ip/Idark)	18.5	13	9.6x10 <sup>2</sup>	2.63x10 <sup>5</sup>
$\tau_{rise}$ (s)	20	<0.1	30	<0.1
$\tau_{fall}$ (s)	>300	<0.1	1.5	<0.1

elevating Ip because neutralization of Vo2+ may require high activation energy. This further supports the severe PPC effect of ZnO and IGZO TFT after light-off. On the other hand, photo-generation by band-to-band rules the photo-dynamic behavior of ZnON TFT considering its optical bandgap (~1.84 eV). This offers the highest probability of recombination by photo-generated electron hole pairs. However, a slight slope of ZnON TFT during light-on was observed, which can be explained from consistent photo-generation by nitrogen vacancy (V<sub>N</sub>). The PPC effect may also arise by the photo-ionized V<sub>N</sub><sup>x+</sup> (x=1, 2, or 3) and gets stronger when ZnON involves excess nitrogen and considerable non-stochiometric Zn<sub>x</sub>N<sub>y</sub> chemical states [14]. However, our ZnON thin film had nitrogen concentration of ~13 at% and was primarily composed of stoichiometric Zn<sub>3</sub>N<sub>2</sub> chemical states. This led to the lowest slope during light-on and negligible PPC

effect after light-off. To evaluate the photo-response, the rise  $(\tau_{rise})$  and fall  $(\tau_{fall})$  time were defined as the time to reach 1/e of the photocurrent (I<sub>p</sub>) after light-on and before light-off. Besides, signal-to-noise ratio (SNR) was defined by Ip/Idark, where Idark represents dark current. Table 1 summarizes device performance parameters where ZnON TFT exhibited extremely short rise and fall time less than 0.1 s. However, ZnON TFT suffered from poor SNR. Thus, IGZO/ZnON TFT was fabricated to get benefit from the high SNR of IGZO and transient response of ZnON. As shown in Fig. 6 (a) and Table 1, the electrical properties were similar to those of IGZO TFT except for positively shifted V<sub>TH</sub> possibly due to thicker ZnON. As shown in Fig. 6 (b), our proposed IGZO/ZnON phototransistor exhibited the best performance in terms of the highest SNR and transient photo-response as well.

Fig. 7. illustrates an energy band diagram of our IGZO/ZnON phototransistor. Effective electric field on the thin IGZO (10 nm) would be strong and electrons photogenerated by Vo states quickly drift to the conduction band minimum (CBM) of ZnON, resulting in high SNR. At the same time, ZnON which has an excellent recombination characteristic by band-to-band enable nearly constant slope during light-on. We also suggest that the accumulated electrons in the CBM of ZnON can recombine with  $V_0^{2+}$  states of IGZO and  $V_N^{x+}$  states of ZnON. The former may be possible since the energy level of electrons has been lowered by drift to CBM of ZnON, providing higher probability to recombine with Vo2+ states of IGZO. The latter is reasonable from the result in Fig. 6 (b), where ZnON phototransistor had the lowest slope during light-on and negligible PPC effect. Thus, accumulated electrons in the CBM of ZnON would recombine with VBM and  $V_N^{x+}$  states of ZnON, and  $V_O^{2+}$ states of IGZO when the light is turned off.



**Fig. 7** A schematic energy band diagram of IGZO/ZnON phototransistor for light on and off state.

## Acknowledgments

This work was supported by the National Research Foundation of Korea (NRF) through the National R&D Program (No. 2021M3F3A2A01037927) and Samsung Electronics Co., Ltd (IO220817-02058-01).

## 4 Conclusions

ZnON thin film was deposited by reactive sputtering of ZnO ceramic target. Optical, structural, chemical characterizations revealed that the nitrogen was successfully incorporated into the fundamental ZnO matrix. The influence of nitrogen was noticeable in TFT characteristics. Electrical properties of ZnON TFT were improved compared with those of ZnO TFT. More importantly, the PPC effect was negligible. Finally, the heterojunction-based phototransistor employing *in-situ* deposition of IGZO/ZnON exhibited transient photoresponse and higher SNR than single ZnO, ZnON, and IGZO phototransistors.

#### References

[1] K.-J. Zhou *et al.*, "Heterogeneous metal oxide channel structure for ultra-high sensitivity phototransistor with modulated operating conditions," *Journal of Materials Chemistry C*, 2022.

[2] Y. Jang, J. Park, J. Kang, and S.-Y. Lee, "Amorphous InGaZnO (a-IGZO) Synaptic Transistor for Neuromorphic Computing," *ACS Applied Electronic Materials*, vol. 4, no. 4, pp. 1427-1448, 2022.

[3] H.-S. Kim *et al.*, "Anion control as a strategy to achieve high-mobility and high-stability oxide thin-film transistors," *Scientific reports,* vol. 3, no. 1, pp. 1-7, 2013.

[4] A. Reinhardt, H. von Wenckstern, and M. Grundmann, "All-Amorphous Junction Field-Effect Transistors Based on High-Mobility Zinc Oxynitride," *Advanced Electronic Materials*, 2021.

[5] T. Kim, M. J. Kim, J. Lee, and J. K. Jeong, "Boosting Carrier Mobility in Zinc Oxynitride Thin-Film Transistors via Tantalum Oxide Encapsulation," *ACS Applied Materials & Interfaces*, vol. 11, no. 25, pp. 22501-22509, 2019.

[6] J. T. Jang, H.-D. Kim, D. M. Kim, S.-J. Choi, H.-S. Kim, and D. H. Kim, "Influence of nitrogen content on persistent photoconductivity in zinc oxynitride thin film transistors," *IEEE Electron Device Letters*, vol. 41, no. 4, pp. 561-564, 2020.

[7] J. T. Jang *et al.*, "Observation of Divacancy Formation for ZnON Thin-Film Transistors With Excessive N Content," *IEEE Electron Device Letters*, vol. 42, no. 7, pp. 1006-1009, 2021.

[8] M. Futsuhara, K. Yoshioka, and O. Takai, "Optical properties of zinc oxynitride thin films," *Thin Solid Films*, vol. 317, no. 1, pp. 322-325, 1998.

[9] T. Yamazaki *et al.*, "Amorphous ZnOxNy thin films with high electron Hall mobility exceeding 200 cm2 V-1 s-1," *Applied Physics Letters*, vol. 109, no. 26, p. 262101, 2016.

[10] Y. Hirose, M. Tsuchii, K. Shigematsu, Y. Kakefuda, T. Mori, and T. Hasegawa, "Thermoelectric properties of amorphous ZnOxNy thin films at room temperature," *Applied Physics Letters*, vol. 114, no. 19, p. 193903, 2019.

[11] E. Lee *et al.*, "Nanocrystalline ZnON; High mobility and low band gap semiconductor material for high performance switch transistor and image sensor application," *Scientific reports*, vol. 4, no. 1, pp. 1-8, 2014.

[12] J. L. Pau, M. J. Hernández, M. Cervera, E. Ruiz, and J. Piqueras, "Properties of zinc oxynitride films deposited by reactive magnetron sputtering at room temperature," in *Proc.SPIE*, vol. 7603, 2010.

[13] J. Srivastava, S. Nahas, S. Bhowmick, and A. Gaur, "Electronic structure and transport in amorphous metal oxide and amorphous metal oxynitride semiconductors," *Journal of Applied Physics*, vol. 126, no. 12, p. 125702, 2019.

[14] H.-M. Lee, H.-J. Jeong, K.-C. Ok, Y. S. Rim, and J.-S. Park, "Near-Infrared Photoresponsivity of ZnON Thin-Film Transistor with Energy Band-Tunable Semiconductor," *ACS Applied Materials & Interfaces*, vol. 10, no. 36, 2018.