Supporting Information for

Combined control of cation and anion to make ZnSnON thin films

for visible-light phototransistors with high responsivity

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S1.The analysis of the TEM

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S1. The analysis of the TEM



Fig. S1. (a)-(c) High-resolution transmission electron microscope (HR-TEM) images and selected-area electron diffraction patterns (SADPs) of 250 $^{\circ}$ C ZSON film. (d)-(f) HR-TEM image and SADPs of 300 $^{\circ}$ C ZSON film. The inset in the left top of figure R1-e shows the corresponding fast Fourier transform (FFT) image. It presents a well-aligned set of hexagonal spots for {01-10} planes of hexagonal ZnO and confirming the presence of ZnO.

The high-resolution transmission electron microscope (HR-TEM) images and selected-area electron diffraction patterns (SADPs) of the 250 °C and 300 °C-annealed ZSON films are shown in Figure S1 a-f. The 250 °C-annealed ZSON film shows a cubic Zn_3N_2 nanocrystallite within an amorphous matrix, very similar to the as-deposited ZSON film. For the 300 °C-annealed ZSON film, the microstructure varies a lot. Some nanometer-sized ZnO grains are observed besides Zn_3N_2 grains. In addition, the crystallinity is enhanced distinctly.







Fig. S2. (a) O 1s and N 1s core-level XPS peaks of 250 °C annealed-ZSON and ZON thin films. Herein, the letter M represents the element Sn or Zn. (b) Auger transition of Zn for 250 °C annealed-ZON thin film. (c) Sn $3d_{5/2}$ core-level XPS spectra of 250 °C annealed-ZSON thin film.

Fig. S2a shows the O1s and N1s core-level XPS spectra of the 250 °C-annealed ZSON and ZON films, including the information from both the surface and the bulk layers (Etching depth is around 10 nm). The O 1s and N 1s spectra can be deconvoluted into several featured peaks, and the corresponding peak positions and specific bonds are presented in the Fig. S2a based on the previous reports.^{\$1,\$2} Fig. S2b shows the Zn L₃M₄₅M₄₅ Auger peaks for the 250 ^oC-annealed ZON film. The peak assignment is roughly determined according to literatures^{s3} and in the Fig. S2b shows the Sn 3d core-level XPS peaks for the 250 °C-annealed ZSON films. Herein, only the Sn $3d_{5/2}$ component is focused on, because the Sn $3d_{5/3}$ component is overlapped with the Zn L₃M₄₅M₄₅ Auger peaks. A refinement of the Sn 3d_{5/2} signal requires the use of three featured peaks in order to model the experimental data properly for both the surface (peak labeled with A, B and C) and the bulk (peak labeled with B, C and D) layer. According to literatures, ^{s4,s5} the binding energies of Sn⁴⁺, Sn²⁺ (bonding to oxygen) and the metallic Sn⁰ state is located at 486.5±0.2, 485.5±0.1 and 483.9±0.1 eV, respectively. However, the incorporation of N would induce 0.3-0.4 eV shift toward lower binding energies. In the surface layer, the peak A (486.7 eV) is definitely assigned to SnO₂ phase, while the peak B at 486.3 eV (C at 485.2 eV) is regarded as the combination of Sn^{4+} (Sn^{2+}) bonding to oxygen and nitrogen. That is to say, Sn in the surface layer is mainly in the form of oxide and oxynitride. In the bulk, the SnO_2 phase (peak A) is completely omitted, while the peak B is still dominated. Due to the presence of fewer oxygen, the peak position of peak B is shifted toward lower binding energy (485.9 eV). In addition, a distinct peak D (484.0 eV) of metallic Sn is observed. It is suggested that the ZSON bulk contains trace content of oxygen, in line with the corresponding O 1s peak in Fig. S2a.

Table S1 Chemical composition of 250 °C annealed -ZSON and ZON thin films, deduced from XPS areas.

Samula	Chemical composition (at%)						
Sample	Zn	Sn	0	Ν			
Surface ZSON	21.66	8.46	65.55	4.33			
Etched ZSON	58.28	9.80	12.60	19.32			
Surface ZON	37.98	-	58.47	3.56			
Etched ZON	70.39	-	13.89	15.72			

S3. The construction of SE fitting model and linear extrapolation of optical bandgap

Table S2 Summary of the fitted results for the ZSON and ZON films on the Si substrates using double Tauc–Lorentz dispersion function. T is the thicknesses of ZSON and ZON film with the unit of nanometer. MSE is the mean-square error.

Sample	Τ	A_1	$E_{\rm g1}$	E_{01}	<i>C</i> ₁	A_2	$E_{\rm g2}$	E_{02}	C_2	MSE
as-dep. ZSON	20.87	38.13	2.60	1.23	3.30	63.22	1.21	6.06	5.78	1.82
200°C-ZSON	20.81	31.77	2.60	1.20	3.30	54.95	1.39	5.79	6.00	1.90
250°C-ZSON	22.18	21.58	2.60	1.18	3.30	49.15	1.38	6.36	7.04	1.78
300°C-ZSON	24.07	3632.9	2.60	0.0001	3.30	49.95	1.81	3.84	12.33	1.98
as-dep. ZON	25.77	58.04	2.60	1.07	3.30	95.56	1.43	6.81	7.81	2.71
200°C-ZON	26.02	58.65	2.60	1.06	3.30	88.54	1.55	7.28	6.54	3.20
250°C-ZON	27.61	29.31	2.60	1.06	3.30	99.62	1.65	7.28	8.50	2.92
300°C-ZON	27.57	29.32	2.60	1.06	3.3	86.40	1.70	7.94	8.31	3.50



Fig. S3. Experimental (symbols) and fitted (solid curves) ψ and Δ of the ZSON film annealed at 300 °C. The ellipsometric angle ψ and phase difference Δ were recorded at the incidence angle of 55, 65, and 75 °.

The optical properties of the films were characterized by a variable angle spectroscopic ellipsometer (SE) in the wavelength (λ) ranging from 200 nm to 1700 nm. A simple three-phase model, i.e., Si substrate/bulk layer/surface layer, was used to fit the SE data. Double Tauc-Lorentz (TL) dispersion functions were employed to generate the absorption coefficient (α) for the bulk layer, and one TL function for the surface layer. The TL dispersion function, as a generic model to describe semiconductor materials, was employed to determine the dielectric function of the ZSON films, as shown in follows^{s6}:

$$\varepsilon_{1}(E) = \varepsilon_{\infty} + \frac{2}{\pi} P \int_{E_{g}}^{\infty} \frac{\xi \varepsilon_{2}(\xi)}{\xi^{2} - E^{2}} d\xi, \qquad (1)$$

$$\varepsilon_{2}(E) = \begin{cases} \frac{AE_{0}C(E - E_{g})^{2}}{(E^{2} - E_{0}^{2})^{2} + C^{2}E^{2}} \frac{1}{E}, & (E > E_{g}) \\ 0, & (E \le E_{g}) \end{cases}$$

Where A is the amplitude, E_0 the peak transition energy, C the broadening term, and E_g the band gap. The detailed parameters are summarized in Table S2.The fitting quality was evaluated based on the mean-squared error (MSE) function. The mean-squared error value is pretty small (< 4), meaning that the fitting accuracy is acceptable (Generally, the fitting quality is acceptable only if the MSE value is less than 10). Moreover, we compared the experimental and fitted spectroscopic spectra of the ellipsometric angle ψ and phase difference Δ for the 300 °C-annealed ZSON film (this sample is with the biggest MSE among all the ZSON films). As shown in Fig. S3, a good superposition between the experimental and fitting spectra is observed, indicating that the double TL dispersion function works very well. Based on the SE fitting results, the optical bandgap parameters of the ZSON and ZON films were obtained, as seen in Fig. S4.



Fig. S4. Plots of $(\alpha hv)^2$ versus hv of (a) ZON and (b) ZSON films.

S4. Dependence of the photoresponsivity on the gate voltage and photoconductivity spectra

Fig. S5a shows the photoresponsivity spectra of the 250 °C-annealed ZSON TFTs in response to the light illumination ranging from 200 nm to 800 nm. The photoresponsivity peak position is corresponding to the gate voltage of 29 V, independent of the wavelength of the incident light. Theoretically, the photoresponsivity is proportional to the field-effect

mobility of the device (*P*hotoresponsivity = $\frac{\eta \mu \pi A F_0 V_D W}{PL}$). For ZSON TFT device in

this article, it's observed that the field effect mobility increases initially to the peak at 29 V and then decreases as the gate voltage increases. The reason why the maximum photoresponsivity is obtained at 29 V is attributed to gate voltage-dependent field-effect mobility. Meanwhile, the photoconductivity σ_{ph} as a function of photon energy is also calculated and shown in Fig. S5b.



Fig. S5. (a) Dependence of the photoresponsivity on the gate voltage for 250°C-annealed ZSON TFTs. (b) Photoconductivity spectra of 250°C-annealed ZSON TFT.

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