## **Supporting Information**

Liquid metal-based Printing Synthesis of bismuth-doped gallium oxide and its application for photodetector

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Structure /method	Bias (V)	Photoresponsivity (A W <sup>-1</sup> )	EQE (%)	Response/ Recovery time (s)	Reference
α-Ga <sub>2</sub> O <sub>3</sub> film /(MBE)	20	0.015	7.39		1
Mn:Ga <sub>2</sub> O <sub>3</sub> film /(MBE)	10	0.07	36	0.91/0.28	2
Ga <sub>2</sub> O <sub>3</sub> film /(MBE)	10	8.41		2.87/0.41	3
Ga <sub>2</sub> O <sub>3</sub> film (MOCVD)	10	1.2			4
Ga <sub>2</sub> O <sub>3</sub> film /(Sol-Gel)	10	0.0013		0.1/0.1	5
Ga <sub>1.8</sub> Sn <sub>0.2</sub> O <sub>3</sub> thin film /(LMBE)	15	0.0065	3.02		6
Bi:Ga <sub>2</sub> O <sub>3</sub> film /(vdW printing)	6	0.959	433	0.013/0.018	This work

Table S1 Performance Comparisons of the  $Ga_2O_3$  film photodetectors in different works



**Fig. S2** The phase diagram of Bi-Ga alloy which adapted from reference.<sup>7</sup> L,  $L_1$ ,  $L_2$  stand for liquid, liquid Bi metal, liquid Ga metal, respectively. The red line indicated that melting point is 200 °C when the content of Bi is 15 wt% in alloy, so we selected the alloy with less than 15 wt% Bi to keep the melting point below 200 °C.



**Fig. S3** (a-c) Optical images (left) and AFM images (right) of printed film. The inset in right shows the thickness of Bi doped oxide film obtained from 0 wt%, 10 wt%, 15 wt% Bi-Ga alloy and the measurement result display an increases trend which from 2.8 nm to 4.6 nm.



**Fig. S4** (a-c) TEM images (left) and EDS mappings (right) of films printed from the surface of 0 wt%, 10 wt%, 15 wt% Bi-Ga alloy. A large, ultrathin and smooth film can be found in TEM images. The EDS mappings display the distribution of Ga, O, Bi element in doped or undoped oxide film. The region of Bi is similar to that of Ga and film, which further confirm both the Bi and Ga atoms exist in the films.



**Fig. S5** TEM image showing a fold edge of printed film because of the excellent flexibility, which is caused by the large area and ultrathin.



**Fig. S6** XPS spectrum of printed film obtained from 20 wt% Bi-Ga alloy. Due to the higher melting point (>200 °C), it is hard to remove residual alloy, so the intensity of the Bi 4f belong to the metal is stronger than that of Bi 4f belong to  $Bi_2O_3$ .



**Fig.S7** The GIXRD data of oxide thin films obtained from the surface of 0 wt%  $\cdot$  1 wt%  $\cdot$  10 wt%  $\cdot$  15 wt% Bi-Ga alloy. The diffraction peaks observed at 36° and 50.2° correspond to gallium oxide, while the peak at 27.4° corresponds to bismuth oxide. The reference PDF standard card numbers for gallium oxide and bismuth oxide used are 06-0503 and 16-0654, respectively. The incident angle was set at 0.3° to ensure minimizing the contribution from the substrate. The diffraction patterns were collected in the 20 range of 10° to 90° with a step size of 0.02° and a scan rate of 10° per minute.



**Fig. S8** (a) UV-Vis transmission spectrum and calculated (b-c) Tauc plots of films printed from 0 wt%, 1 wt%, 10 wt% Bi-Ga alloy. The bang gaps are determined as 5.23 eV, 5.05 eV, 4.94 eV through a tangent line, respectively.



Fig. S9 I-V curve of printed film obtained from 15 wt% Bi-Ga alloy under 0.8 mWcm<sup>-2</sup> UV light.



**Fig. S10** (a) I-V curves of printed films obtained from 0 wt%, 1 wt%, 10 wt%, 15 wt% Bi-Ga alloy under UV light (275 nm, 0.8 mW cm<sup>-2</sup>). (b) I-T curve of printed films obtained from 0 wt%, 1 wt%, 10 wt%, 15 wt% Bi-Ga alloy under UV light (275 nm, 0.8 mW cm<sup>-2</sup>). (c) The I-T curve of printed film obtained from 15 wt% alloy under natural light and UV light (275 nm, 6 V). (d) The photoresponsivity (right) and  $I_p$  (left) of oxide films under 6 V, 275 nm, 0.8 mW cm<sup>-2</sup>, which were printed from 0 wt%, 1 wt%, 10 wt%, 15 wt% Bi-Ga alloy.

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