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Gas-mediated liquid metal printing toward large-scale 2D semiconductors and ultraviolet photodetector

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A gas-mediated fabrication of centimeter-scale two-dimensional (2D) semiconductors and ultraviolet photodetector by a liquid metal-based printing was reported. Various large-scale 2D materials (Ga_2O_3 , In_2O_3 , SnO) were demonstrated to be directly printed at ambient air on different substrates. Such printing represents a generic, fast, clean, and scalable technique to quickly manufacture 2D semiconductors. The electrical properties were explored to quantify the printed 2D films, which were somewhat deficient in previous studies. In particular, to explore and facilitate the advantages of this 2D semiconductor in functional electronic applications, strategies for realizing fully printed $\text{Ga}_2\text{O}_3/\text{Si}$ heterojunction photodetector via low-temperature and low-cost processes were developed. The device exhibits excellent sensibility and rapid photoresponse times. This work offers feasible way to develop high-performance ultraviolet photodetector for mass production. It also suggests a promising direction for making large-scale 2D photoelectronic and electronic systems and is expected to be extensively useful in the coming time.

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INTRODUCTION

Two-dimensional semiconductors with good vectors mobility as well as excellent mechanical features are ideal materials for modern generation electronics, especially for flexible electronics, extensive area, and optoelectronics. However, large-scale production of low-cost flexible electronic products requires a simple and effective strategy of deposition and patterning of these materials¹. Up to now, several methods have been demonstrated to separate and synthesize two-dimensional materials. The simplest method is to mechanically remove the atomic sheets from the lamellar crystal with tape². This allows high crystallinity flakes to be made, but the yield is pretty low. In addition, these sheets are irregular in shape and only tens of microns in length, so they are not appropriate for practical use in large-scale. Chemical vapor deposition³ and metal-organic chemical vapor deposition (MOCVD)⁴ have made great progress as a method for large area growth of two-dimensional material samples. In these approaches, one or more volatile precursors are utilized in order to decompose or react above the surface of the layers to deposit the required materials. The aforementioned approaches allow materials to grow on a rigid substrate including sapphire and silica, with an area of about tens of square centimeters. But these processes need almost high temperatures (above 550 °C), that limits the growth on polymer substrates with high flexibility. In addition, the long growth time entailed (around 26 h for centimeter-scale MOCVD growth) is a pervasive problem for manufacturing on mass scale.

Liquid metals have numerous interesting surface and bulk properties, which have attracted great attention in various engineering applications, including microfluidic components⁵, sensors⁶, electrodes⁷, transistors⁸, flexible and scalable systems⁹, disease therapy¹⁰, and biomedical area¹¹. In particular, under atmospheric conditions, liquid metal displays a naturally formed atomic thin oxide layer on its interface. This kind of metal oxide can adhere well to other oxides (such as silicon dioxide and

silicon) which are usually used as substrates of electronic devices, but the parent metal in a liquid state cannot. It has been gradually realized that liquid metals have a wide melting range and can form a variety of alloys. Furthermore, the skin of the alloys can be adjusted, which brings opportunities for the preparation of various 2D films. By contacting the liquid metal droplet with the target substrate, various binary metal oxide thin sheets, such as Ga_2O_3 ¹², Bi_2O_3 ¹³, SnO ¹⁴, and SnO_2 ¹⁵, can be obtained by using the skin of the liquid metal. Some studies further found that the surface oxides formed on the In-Sn alloy contain In and Sn with a ratio similar to that of indium tin oxide (ITO). Therefore, by stripping the surface of this alloy, wafer-scale ITO sheets with thicknesses of only a few atoms were successfully prepared¹⁶. In addition, through the post-processing steps, the skin of liquid metal can also be used to manufacture other 2D films, such as GaPO_4 ¹⁷, GaN ¹⁸, GaS ¹⁹, and Ga_2S_3 ²⁰, and microscale 2D single crystals, such as Mo_2GaC ²¹, GaN ²², whether they are essentially layered or non layered materials. Moreover, transition metal oxides (HfO_2), post-transition metal oxides (Al_2O_3), and rare earth metal oxides (Gd_2O_3) can also be prepared on the surface of liquid metal alloy by alloying HF, Al, and Gd with galinstan, respectively²³. However, the characterization of electrical properties of these 2D oxide films is still scarce, and there are few reports on the fabrication of semiconductor functional devices using 2D oxide films.

In this article, different to conventional techniques, we report the fully printed ultraviolet (UV) solar-blind photodetector based on printed 2D oxide films and Si heterojunction. In order to prepare two-dimensional oxide films suitable for optoelectronic devices, we adopted low-temperature printing technology of wafer-scale 2D semiconductor films. Through melting metal on substrates and scraping printing the metal, we are able to transfer a slim layer of metal oxide onto the target layers. This technique works just like the process of applying ink to paper or fabric in printing of screen. Using such print technology, we have manufactured large-scale high-quality 2D semiconductor films

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on different substrates. A series of characterizations of printed 2D semiconductor materials were carried out, especially the electrical properties and optical absorption properties which were insufficient in previous studies. Furthermore, we analyzed and explored three kinds of printed 2D semiconductor, and chose Ga_2O_3 with the best light absorption characteristics to construct ultraviolet photoelectric devices. Different from traditional and conventional techniques, we demonstrate the fully printed ultraviolet (UV) solar-blind photodetector by printing n-type Ga_2O_3 film over p-type Si, the p-n vdW heterojunctions property current rectification features with rapid photoresponse times and good sensibility for UV resource, which provides the performance of detection attributed to the solar-blind with stable and susceptible performances. The demonstrated liquid metal print framework reveals convenient and effective pathways for the preparation of 2D semiconductor photodetector that are vast area, cheap, and appropriate for mass production. Moreover, lower preparation temperature makes it possible for the printing process to be used on highly flexible polymer substrates such as polyimide in the future, which renders the possibility for an extensive spectrum of applications in next-generation of photodetection and optoelectronic instruments.

RESULTS AND DISCUSSION

Liquid metal-based 2D semiconductors print

Our printing process relies on the effective transfer and adhesion of oxide thin layers on metal surface. As shown in Fig. 1, the preparation process is divided into two steps: melting the metal and scraping off the parent metal of liquid metal. The oxide scale of liquid metals (Ga, In, and Sn) is atomic thin and has a weak binding force with the parent metal. It could be readily transferred and adhered to the required substrate by van der Waals force. Residual small metal droplets are removed by a solvent-assisted mechanical and chemical cleaning. Van der Waals force ensures that the oxide film adheres firmly to the substrate surface. After the completion of the whole process, large and continuous two-dimensional semiconductor (metal oxide) thin films with a transverse scale of more than several centimeters can be obtained (details in “Experimental” section).

Characterizations of 2D semiconductors $\text{Ga}_2\text{O}_3/\text{In}_2\text{O}_3/\text{SnO}$

In order to select suitable 2D semiconductors films for optoelectronic devices, we measured the morphology and structural characterization of the printed 2D Ga_2O_3 , In_2O_3 , and SnO films on

a SiO_2/Si substrate, as shown in Fig. 2. The optical image of the semiconductor films is shown in the left part of Fig. 2, which indicates all films revealed lateral dimensions of several millimeters to near centimeters. The morphology of the surface and thickness of the printed films were surveyed through atomic force microscopy (AFM). Owing to the restricted scanning region size of AFM, a sole tiny part of the super gross semiconductor film is shown in the center of Fig. 2, which confirms the successful transfer and printing of the semiconductor layer. For the printed 2D Ga_2O_3 films, the regular step height between the substrate and the Ga_2O_3 film is about 4.1 nm, which is slightly thicker than the previously published sheet separated by liquid metal printing technology. Local metallic inclusions only occasionally appear at the edge of the large film. Each type of the 2D films prepared by this process has a different thickness: 4.1 nm for Ga_2O_3 , 3.2 nm for In_2O_3 , and 4.4 nm for SnO. It has been proven by experiments that the printing technology can reproduce the formation of uniform centimeter-scale semiconductor films on different substrates (Supplementary Fig. S1). Relatively speaking, the quality of printed semiconductor film on SiO_2/Si surface is optimal, so the subsequent characterization and device preparation are based on the 2D film printed on SiO_2/Si surface.

High-resolution transmission electron microscopy known as (HRTEM) was utilized for illuminating the crystal configuration as well as structural properties attributed to the printed films. The right side of Fig. 2 shows the TEM image of the printed 2D semiconductor, the inset is a pattern of the selected area electron diffraction (SAED) of the chosen studied region. In Fig. 2a, it can be observed that the lattice spacing is 0.46 nm, according to the d-spacing value of the (201) plane of Ga_2O_3 . From the HRTEM illustration and SAED pattern of In_2O_3 in Fig. 2b, we can see that there exist two latticed d-spacing in the film. The d-spacing of 0.25 nm conforms to the (400) plane, whilst the other 0.28 nm d-spacing is attributed to the (222) face of In_2O_3 . For SnO, the d-spacing of 0.26 nm conforms to the (110) plane of SnO (Fig. 2c). We also analyzed the X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) of various oxide films to check the purity of the printed semiconductor films. XPS results show that there are only pure Ga_2O_3 , In_2O_3 , and SnO in the 2D oxide films, but no metal elements and/or other oxides (see Supplementary Figs. S2 and S3 for detailed analysis). XRD results show that all the 2D oxide films have a good lattice structure, which matches well with the peak position of the standard spectrum (see Supplementary Fig. S4 for detailed analysis). The attained XPS data and the other characterization techniques aforementioned above provide the outcome that all of our printed 2D semiconductor materials have

Fig. 1 Schematic of the 2D semiconductors printing process. Liquid metal can form atomic thin-layer metal oxides under atmospheric conditions. When the liquid metal was scraped amongst the surface of the silica layer with the “squeegee”, the liquid parent metal is cleared off, however, the layer of oxide adheres to surface of the substrate to achieve a large-scale thin layer of the semiconductor.

Fig. 2 Morphological and crystalline characterizations of the print 2D semiconductors. **a–c** optical images exhibit homogeneous films featuring lateral dimensions spanning multiple centimeters (scale bar, 0.5 mm). **d–f** AFM illustrations, with thickness profile (inset) specified at the red line as illustrated (scale bar, 5 μ m). **g–i** TEM characterization of the print semiconductors, including HRTEM images (scale bar, 0.5 nm) and SAED pattern of the corresponding region (bottom inset).

good consistency and can be used for further characterization of electrical and photoelectric properties.

Electrical and optical absorption characterization of printed 2D semiconductor material

Due to the difference between 2D films prepared by printing and CVD, which may have some influence on the electronic and optical characteristics. First, we need to further explore the optical absorption characteristics of three 2D oxide materials prepared by printing method. The measured optical absorption results of Ga₂O₃, In₂O₃, and SnO films are shown in Fig. 3a. They revealed that the Ga₂O₃ film demonstrates potent absorption in the spectral area less than 250 nm, and is approximately transparent in the spectral scope of 260–800 nm, which indicates that the film has significant absorption in the ultraviolet area, particularly in the solar-blind area, it is an excellent material for fabricating UV detectors. The In₂O₃ thin film has strong absorption ability to the ultraviolet light less than 400 nm, but it also owns certain absorption ability to the violet light of 400–455 nm and the blue light of 455–492 nm. The optical absorption band of SnO film have extended to the ultraviolet radiation B region, in addition, the film exhibits a weak absorption in the solar-blind region. The ideal solar-blind UV photodetectors request that the devices have no response to the light with wavelength above 280 nm²⁴. Therefore, for the construction of photodetector devices, the optical properties of Ga₂O₃ films are significantly better than those of In₂O₃ and SnO.

Ga₂O₃ is a direct bandgap semiconductor material²⁵, so we evaluate the bandgap of the Ga₂O₃ films based on the spectrum of absorbance related to the Ga₂O₃ thin film. The corresponding bandgap energy (E_g) can be estimated by Tauc's analysis based on the equation.

$$(ah\nu)^2 = C \cdot (h\nu - E_g) \quad (1)$$

In this equation, h represents the Planck constant, a stands for the linear coefficient of absorption, ν states the photon frequency, and C is the constant. As exhibited in the illustration of Fig. 3b, via fitting the linear region between $(ah\nu)^2$ and the photon energy $h\nu$ axis, the bandgap of printed Ga₂O₃ is evaluated about ≈ 4.8 eV, which is in good agreement with the indirect transition of double-layer Ga₂O₃, which further proves the uniformity of the film. Figure 3c shows a plot of $(ah\nu)^2$ vs. $h\nu$ based on UV–vis absorption spectra of printed 2D In₂O₃. The Tauc plots diagram achieved by the analysis of UV–vis shows that the bandgap of 2D In₂O₃ is ~ 3.1 eV, indicating that the film has a nearly inherent behavior. Similarly, the direct E_g for the printed SnO film was evaluated about ~ 3.7 eV, near the already achieved outcome E_g for tetragonal SnO (~ 3.7 eV)²⁶. The $(ah\nu)^{1/2}$ vs. $h\nu$ plot shows the existence of an indirect bandgap of ~ 2.2 eV (Fig. S5). A first-principle calculation suggests that the indirect bandgap is about 1.6 eV smaller than the direct bandgap²⁷, which is approximate to our current experimental values. For such printed SnO, the value of indirect bandgap is a little larger than most of the general SnO. We speculate that the quality of the film (such as crystallite size, number of structural defects, chemical

Fig. 3 The material properties and electronic band characterizations of printed 2D semiconductor. **a** The spectrum of the absorbance related to the printed Ga_2O_3 , In_2O_3 , and SnO films. Tauc plot utilized in order to specify the electronic band gap for **b** Ga_2O_3 , **c** In_2O_3 and **d** SnO with a clarified electronic band plot.

Fig. 4 The electrical properties of 2D semiconductor films. The evaluated UPS spectrum obtained from the printed **a** 2D- Ga_2O_3 , **b** In_2O_3 , and **c** SnO to identify their electron affinity value.

composition, etc.^{28,29}) has a strong influence on the optical properties near the absorption edge.

In semiconductor electronic devices, the carriers are injected into the semiconductor from the electrical contact, and the devices utilize the fine control of the flow of the carrier. In theory, the work function represents the minimum energy required for the electron to escape from the material to the free space, and the electron affinity is the energy released when the electron falls from the free space to the bottom of the semiconductor conduction band. These parameters can provide important theoretical basis for exploring the contact properties between metal and 2D semiconductor, and the contact properties determine the performance of the device. Therefore, further research on the intrinsic electrical characteristics of 2D semiconductor is very important for the performance of 2D electronic and optoelectronic devices.

Ultraviolet photoelectron spectroscopy (UPS) is a common method to characterize the electrical properties of the 2D semiconductor films, it was carried out in an ultra-high vacuum system supplied within the light resource of specs microwave ultraviolet ($\text{HeI} = 21.2 \text{ eV}$; UV spot diameter is around 1 mm). The UPS spectrum of the printed 2D semiconductor is shown in Fig. 4, which presents the cutoff region and the edge region of the valence band. By calculation, the conforming maximum value of valence band (VBM) value of Ga_2O_3 is 5.21 eV, while the electron affinity of printed Ga_2O_3 is 3.5 eV. Similarly, In_2O_3 thin films exhibit $\text{VBM} = 6.03 \text{ eV}$, and the VBM energy of SnO is calculated to be 5.23 eV. The electron affinity of In_2O_3 and SnO are calculated as 2.9 and 3.8 eV, respectively. (See Supporting material for detailed calculation process) These results agree with the theoretical very well, indicating that the printed Ga_2O_3 , In_2O_3 , and SnO films have good electrical properties. Considering the optical absorption

Fig. 5 Schematic image and energy band diagrams of the fully printed $\text{Ga}_2\text{O}_3/\text{Si}$ heterojunction photodetector. **a** Fabrication process of the photodetector. Band diagrams of n-type Ga_2O_3 and p^{++}Si heterostructure indicating **b** pre-junction creation, **c** post junction creation, and **d** under 254 nm illumination.

characteristics, band gap, VBM and electron affinity of the material, the printed Ga_2O_3 film is very suitable for the preparation of solar-blind UV photodetector. Therefore, we constructed and explored the photoelectric detector based on Ga_2O_3 .

Fully printed $\text{Ga}_2\text{O}_3/\text{Si}$ heterojunction UV solar-blind photodetector

Over the recent decades, photodetectors working within the ultraviolet (UV) solar-blind zone (220–280 nm) have attracted extensive attention in military and civil fields. In the present research, we fabricated a good responsivity fully printed solar-blind UV photodetector founded on $\text{Ga}_2\text{O}_3/\text{Si}$ p–n heterojunction via printing n-type Ga_2O_3 on p-type Si. The electrical and optical features of the created p–n heterojunction photodetector were investigated systematically, indicating the great potential of fully printed Ga_2O_3 -based (opto) electronic devices.

The manufacturing process of the fully printed UV solar blind detector was depicted in Fig. 5a. The cleaned $\text{SiO}_2/\text{p}^{++}\text{Si}$ (300 nm/500 μm) substrate was relatively coated with photoresist and then immersed in the etchant buffer oxide (6:1 diluted HF, BOE, j. t. baker) for 5 min. The subjected SiO_2 was etched wetly to disclose potential p^{++}Si , and the etching quality was verified by measuring the resistance of the sheet by applying a four-probe connected to the source surface (Keithley 2400). Ga_2O_3 film was printed on patterned $\text{SiO}_2/\text{p}^{++}\text{Si}$. As demonstrated in Fig. 5a, one end of the deposited Ga_2O_3 creates a p–n junction with p^{++}Si within van der Waals effect, and the other end is completely isolated by SiO_2 and Si. Finally, the fabrication of $\text{Ga}_2\text{O}_3/\text{Si}$ heterojunction photodetectors is completed by printing silver electrodes.

To attain a deep understanding of the pivoting role of the $\text{Ga}_2\text{O}_3/\text{Si}$ heterojunction in ameliorating the optoelectronic performance and

display the operation mechanism in the studied photodetector, the diagrams of energy band related to the $\text{Ga}_2\text{O}_3/\text{Si}$ heterojunction with dark circumstance and UV illumination are both indicated in Fig. 5b–d. Because the gap width of Ga_2O_3 is 4.8 eV, the carrier concentration of Ga_2O_3 film is remarkably less than that of p-Si, a p–n junction is created. We used the Anderson's model to explain the band diagram of $\text{Ga}_2\text{O}_3/\text{p-Si}$ heterojunction³⁰. The values of the conduction band offset (ΔE_{CB}) and valence band offset (ΔE_{VB}) were determined using Anderson's rule (Fig. 5b–d). According to the difference of electron affinity between Ga_2O_3 (3.5 eV) and Si (4.05 eV), ΔE_{CB} was estimated to be 0.55 eV. Based on the band gaps of 4.8 and 1.12 eV for Ga_2O_3 and Si, the ΔE_{VB} value was calculated to be 3.68 eV. Considering all the values, the band diagrams of Ga_2O_3 and Si before and after junction formation are shown in Fig. 5a, b, respectively. When Ga_2O_3 is applied with a positive voltage, the depletion layer composed of Ga_2O_3 layer will expand. Since the impedance of Ga_2O_3 is far greater than that of Si, almost all voltages are applied to Ga_2O_3 . As displayed in Fig. 5c, when $\text{Ga}_2\text{O}_3/\text{p-Si}$ heterojunction is irradiated by 254 nm ultraviolet light, its photon energy is sufficient to excite the carrier of Ga_2O_3 , the carrier generated by light excitation gets high energy under the acceleration of a large electric field in the junction region, and then collides with other atoms in the ionization junction region to generate carriers, and the avalanche multiplication effect is obtained. The electrons can be easily transferred into p-Si to obtain high photocurrent and responsivity. Therefore, the photocurrent of $\text{Ga}_2\text{O}_3/\text{p-Si}$ heterojunction increases exponentially with the applied voltage after being irradiated by 254 nm UV light. It is understood that the instrument has only the following ideal response wavelength of 254 nm. However, the ultraviolet energy at 365 nm is not sufficient to excite the electrons in the valence band of Ga_2O_3 , and the above gain phenomenon will not occur. Therefore, the heterojunction photodetectors have solar-blind ultraviolet characteristics. When a negative

Fig. 6 Characterization of the fully printed UV photodetector founded on Ga₂O₃/Si heterojunction. **a** The linear-scale I–V features in the dark and under 254 nm and 365 nm UV light resources of 100 μW cm⁻². **b** The 254 nm UV light responsivity and the efficiency of external quantum at various implemented voltages. **c** Reproducible on/off switching of photodetector cell under 254 nm light at 10 V. **d** Time-resolved photocurrent assessments under laser resources. The green-shaded areas exhibit laser illumination for 20 s. **e** Time response of Ga₂O₃/Si photodetector. **f** Photoresponsivity and photodetectivity as a function of the great intensities at 10 V.

voltage is exerted to Ga₂O₃, the depletion layer is approached, since the intercepted barrier electrons and holes cannot be transported into p-Si.

We thoroughly investigate the electrical and photoelectric performance of the Ga₂O₃/Si heterojunction device. Figure 6a indicates the current–voltage (I–V) properties of the photodetector instrument impacted by various circumstances, the voltage is applied between the two Ag electrodes. A 254 nm low voltage lamp was utilized as an ultraviolet light source. It can be seen from the results that the reverse current density is tinier than the applied forward one, confirming the creation of junction hindrance. (The Ag electrode on Ga₂O₃ is connected to 0 V, and the voltage applied to the Ag electrode on p-Si is higher than 0 V, which is called forward voltage.) Around the bias of 10 V, the photodetector shows a dark current as low as 9.41×10^{-3} μA,

whilst the corresponding photocurrent is around 8.1 μA, which is about 10³ times higher than the dark current. The current of low dark and high ratio of $I_{\text{photo}}/I_{\text{dark}}$ show that the detector has a notable ratio of signal-to-noise. The photocurrent at 365 nm is approximately equal to the dark current, indicating that Ga₂O₃/Si heterojunction has no response to 365 nm wavelength (UV-A) (inset of Fig. 6a). The response of the device to the wavelength of 254 nm (UV-C) shows that the Ga₂O₃/Si heterojunction is solar blind. In particular, because of the p–n junction structure used in our optoelectronic devices, it can display the function of UV photodiode and photodetector at the same time. So it has significant advantages in complex photoelectric systems such as multi-functional optoelectronic applications.

For the aim of a quantitative assessment of the behavior of photodetectors, the peak responsivity (R) at applied bias voltage is

studied in Fig. 6b, and the light intensity is $100 \mu\text{W cm}^{-2}$. Responsivity is described through the Eq. (2):

$$R = \frac{I_\lambda - I_d}{P_\lambda S} \quad (2)$$

In the aforementioned equation, I_λ states the photocurrent, I_d represents the dark current, P_λ states the light intensity and S is the area of efficient illumination (0.18 mm^2). As illustrated in Fig. 6b, the responsivity of the peak related to the photodetectors improves linearly with the increase of implemented bias voltage. The maximum responsivity can reach 44.6 A W^{-1} at 10 V voltage and $100 \mu\text{W cm}^{-2}$ light intensity. The results show that the photodetector has good spectral response to the solar-blind light. The external quantum efficiency (EQE) is the other essential performance index of photodetectors, it could be explained by the Eq. (3)³¹:

$$\text{EQE}(\eta) = \frac{hcR_\lambda}{q\lambda} \quad (3)$$

where h represents the Planck constant, c is the light speed, q is the charge of an initial electron ($1.6 \times 10^{-19} \text{ C}$), λ states the wavelength of incident ultraviolet light (254 nm), and R_λ is the response to a specific ultraviolet wavelength. Figure 6b also shows the change of EQE of photodetector with applied bias voltage under 254 nm illumination. For our device, the peak responsivity at 254 nm is around 44.6 A W^{-1} , and the corresponding EQE value is as great as $2.2 \times 10^4 \%$ (at 10 V bias), which indicates that the photodetector and resources of ultraviolet light are well-coupled and can be used for UV detection³². Alike to the trend of R , EQE enhances with the increase of implemented voltage under forward bias voltage, which indicates that the photodetector has a great gain³³.

In evaluating photodetectors, response time is an important basic characteristic, especially in applications requiring a fast light response. The time-dependent photocurrent curve ($I-t$) of photodetectors was appraised via periodically turning on and off the light switch. During the measurement, we repeatedly turn on and off the 254 nm, $100 \mu\text{W cm}^{-2}$ UV light source at 20 s interval. Figure 6c shows the transient reaction of the $\text{Ga}_2\text{O}_3/\text{Si}$ photodetector. A time-dependent optical response was obtained at a forward bias voltage of 10 V. The photocurrents time-resolved ($V = 0$ and 10 V) of 20 s before and after laser irradiation were also measured to study the photodecay time (τ_{decay}) (Fig. 6d). As presented in Fig. 6c and d, the current improves instantaneously from $\sim 0.6 \text{ nA}$ to $\sim 8.1 \mu\text{A}$ under illumination, and rapidly decays to $\sim 0.8 \text{ nA}$ when the light source is turned off.

In addition, under 365 nm illumination, we hardly observe the photocurrent change (Supplementary Fig. S6), which is superior to other reported Ga_2O_3 photodetectors with certain response to 365 nm wavelength^{34–37}. Theoretically, when there are deep level defects, the detector can absorb wavelengths longer than the bandgap energy. The detector has no obvious light response at 365 nm, which proves the high quality of printing materials and the excellent combination between Ga_2O_3 and Si.

The reaction speed is another critical criterion of photodetectors, which is about the effective extraction of photogenerated carriers. The time-resolved response of the instrument is further investigated using an additional femtosecond pulse laser as well as an oscilloscope at 266 nm. The results are shown in Fig. 6e. The rise time (τ_r) and the falling time (τ_f) exerted to observe the sensitivity and response. For a more detailed study, the transient response curve is fitted by exponential relaxation equation as follows:

$$I = I_0 + Ae^{-t/\tau} \quad (4)$$

where I_0 shows the photocurrent in a stable state, A represents a constant, t stands for the time, and τ states the constant of relaxation time. τ_r and τ_f represent the increase and decrease

edges of the time constants, respectively. As displayed in Fig. 6e, the photoresponse treatment could be well-fitted with τ_r of 0.2 ms and τ_f of 2 ms. The procedure of fast decay could be ascribed to band-to-band transition, whilst the reduced speed one is attributed to the transition included within the traps³⁸.

The detectivity (D^*), which implies the potential of detection the weak signals from a noisy ambient, is one of the most important features of a photodetector that explains the least number of detectable signals. Definitely, this benchmark is stated as follows³⁹:

$$D^* = \frac{R_\lambda}{\sqrt{2qI_d/S}} \quad (5)$$

Due to the repressed dark current and improved responsivity, considering that $R_{254} = 44.6 \text{ A W}^{-1}$ and $I_d = 4.6 \times 10^{-5} \mu\text{A}$, the D^* value of the $\text{Ga}_2\text{O}_3/\text{Si}$ heterostructure photodetector could be measured to be $3.45 \times 10^{13} \text{ cm Hz}^{1/2} \text{ W}^{-1}$ (Jones) at the wavelength of 254 nm, exhibiting a potent capability of the photodetector to ascertain the normalized signal-to-noise behavior. We further characterized the responsivity and detectivity by different light intensities (Fig. 6f). The fully printed $\text{Ga}_2\text{O}_3/\text{Si}$ photodetector exhibited competitive photoresponsivity and photodetectivity.

Table 1 indicates a comparison of the Ga_2O_3 photodetector fabricated by our group, together with other works, the important parameters are given in the table. It could be observed from the comparison that the $\text{Ga}_2\text{O}_3/\text{Si}$ detector constructed by us shows some encouraging and excellent performance. Some key parameters are better than the instruments founded on Ga_2O_3 ^{40,41}, PEDOTs/ Ga_2O_3 ⁴², graphene/ $\beta\text{-Ga}_2\text{O}_3$ ^{43,44}, and some devices made of AlGaIn^{45,46}, MgZnO^{47,48}, and ZnO^{49,50} et al. Although compared with the best performance photodetectors, there are still some differences in some parameters, but our work adopts the fully printing method based on liquid metal. Compared with other methods, it has great advantages in the rapid preparation of large-area semiconductor films, which is critical for the construction of large-scale and complex photoelectric systems. In addition, our process does not require a high-temperature process, which means that it is feasible to print semiconductor films on flexible polymer substrates such as PI. The liquid metal and the semiconductor films are heat-resistant, which means that this method can also be used in high-temperature manufacturing processes such as chip processing. This technology has the possibility to be extended to the application of flexible photoelectric system and high-temperature photoelectric detection. In summary, the partially great behavior, along with simple, facile fabrication and inexpensive represents the fully printed photodetector promising desirable potential expectancy for producing flexible high-speed optoelectronic systems. Moreover, our devices may further develop in the implementation of the hybrid circuit scheme based on low dimensional materials and should pave the way to develop print large-scale, low-cost, and desirable performance photoelectric systems in the future.

Liquid metals have different potential functionalities. A pretty important value of this series of materials is that they can be adopted to print two-dimensional semiconductor materials with wide applications. In the present work, large-scale high-quality thin 2D semiconductor films have been demonstrated on different substrates using a scalable and facile printing method, through transferring the occurring oxide skin of liquid metal formed under certain conditions. Moreover, we have carried out a thorough interpretation and analysis on the electrical properties of printed 2D semiconductor films, providing key guidance for further development of functional liquid metal printed electronics.

In particular, we successfully exhibited the fully printed solar-blind photodetector based on $\text{Ga}_2\text{O}_3/\text{Si}$ p–n junction, which shows a pretty high responsivity and super detectivity for solar-blind ultraviolet light detection. Such high efficiency, simple, large-

Table 1. Comparison of the most essential criteria of the photodetectors achieved in the current and previous investigations.

Photodetector	Responsivity[A W ⁻¹]	Detectivity [Jones]	On–off ratio	EQE (%)	$t_{\text{rise}}/t_{\text{decay}}$	Ref.
Si/Ga ₂ O ₃	44.6@10 V	3.4×10^{13}	10 ⁵	2.2×10^4	0.2/2 ms	This work
β-Ga ₂ O ₃	1000@3 V	—	10 ⁶	—	—	40
β-Ga ₂ O ₃	8.9@15 V	3.3×10^{13}	—	0.4×10^4	15 μs/1.7 ms	41
PEDOTs/Ga ₂ O ₃	2.6@0 V	2.2×10^{13}	10 ⁴	—	0.34/3 ms	42
Graphene/β-Ga ₂ O ₃	39.3@20 V	5.92×10^{13}	10 ⁴	1.9×10^4	94.83/219.19 s	43
Graphene/β-Ga ₂ O ₃	12.8@6 V	1.3×10^{13}	10 ⁴	—	1.5/2 ms	44
AlGaIn	0.233@10 V	$4. \times 10^{14}$	10 ⁵	45.5	0.22/14.1 s	45
AlGaIn	1.42@10 V	—	1000	—	—	46
MgZnO/Al/ZnO	12@5 V	5.26×10^{10}	—	363	3.52/3.46 s	47
TiO ₂ : GDY/MgZnO	0.00041@10 V	8.1×10^8	—	—	3.5/2.7 s	48
Si/ZnO	101.2@-5V	6×10^{12}	4000	0.7×10^4	0.44/0.59 s	51
p-Si/graphene/n-ZnO	—	—	10.71	—	1.02/0.34 s	49
WS ₂ /Si	0.51@9 V	1.93×10^9	300	101	4.1/4.4 s	52
Graphene quantum dots/ZnO nanorods/GaN	0.034@10 V	$\sim 10^{12}$	—	—	0.1/0.12 s	50
CH ₃ NH ₃ PbCl ₃	0.0496@15 V	1.2×10^{10}	10000	—	24/62 ms	53
CH ₃ NH ₃ PbI ₃	12@4 V	$\sim 10^{11}$	100	0.6×10^4	2.2 ms/4 ms	54

size, and inexpensive manufacturing process suggests a way with great commercial potential for advancing UV photodetectors with diverse engineering values. The advantages as offered may make the two-dimensional semiconductor thus produced as preferred material in printing various flexible optoelectronic devices, which provides a very potential paradigm for future electronics, sensors, and more functional devices.

METHODS

Materials

Gallium (Ga, 99.99%), tin (Sn, 99.8%) and indium (In, 99.98%) were obtained from Roto Metals. Silver nanoparticle inks were obtained from Shanghai Mifang Electronic Technology Co., Ltd.

Printing process of 2D semiconductor films

Ga₂O₃: A self-restricting atomically slim gallium oxide shell creates on the surface of gallium drops as they experienced exposure to atmospheric air. Gallium melts at 29.76 °C, a droplet of gallium collected utilizing a needle was located on a SiO₂/Si substrate. The SiO₂/Si substrate with gallium droplets on the surface is placed on a hotplate, the complete printing procedure was performed on the hotplate with temperature adjusted at 200 °C. The 2D oxide films altered dimensionally with the droplet diameter. At heating condition, a scraper is used to gently scrape the droplet from one end of the substrate to the other, the gallium oxide film could be transfer printed to the substrate. If additional force is utilized during the squeezing level, the oxide layer may be damaged. High-quality Ga₂O₃ films with a transverse dimension larger than several centimeters can be printed on the substrate effectively by this extrusion printing method.

In₂O₃ and SnO: First, the SiO₂/Si substrates were all preheated to 250 °C to refrain from nucleation of the liquid metal upon contact. Secondly, indium metal with high purity was melted on the substrates provided at the same temperature. Thirdly, we use the same printing method to transfer the 2D In₂O₃ oxide films to the SiO₂/Si substrate. The print of 2D SnO films comprises a similar three-step process.

Mechanical and chemical cleaning process

A facile mechanical ethanol cleaning approach was utilized to erase any liquid metal components remaining on the sample. First, take about 100 ml of ethanol in a beaker, then heat the beaker on a heating plate to 100 °C. The substrate with printed 2D oxide film is then immersed in hot ethanol with tweezers. Metal residues are removed by wiping the substrate immersed in ethanol using a wiping tool (swab). There is a potent van der Waals adhesion amongst the oxide film and the bottom layer, and the

oxide film still adheres to the silicon oxide surface during wiping proceeding. On the other hand, there is only a weak adhesion among the deposited oxide and the liquid metal and film, which can be easily erased to keep the 2D film clean and intact. Further, in order to completely and thoroughly remove the metal residue on the substrate, we use a chemical process to clean the samples. An Iodine/triiodide (I⁻/I₃⁻) solution (100 mmol L⁻¹ I⁻ and 5 mmol L⁻¹ I₃⁻) was prepared in ethanol and then placed on a hot plate to heat till 50 °C. The substrate printed with 2D-semiconductor film was immersed in a heated I⁻/I₃⁻ solution for a period of time to completely remove metallic inclusions. Finally, the sample was cleaned in deionized water to remove the residual etchant. The above two cleaning processes can remove liquid metal particles conveniently and effectively.

Characterization

In order to determine the features of the 2D semiconductor thin film and the behaviors of the constructed instruments, various assessments were carried out. The AFM images were employed by a Bruker Dimension Icon with “Scanasyst-air” AFM tips. The high-resolution TEM images were taken utilizing JEOL 2100F TEM operating with 100 keV electron beam energy. XRD was taken utilizing Bruker D8 micro-diffractometer supplied with a detector model Vantec 500 and 0.5 mm collimator. XPS analysis was conducted by Thermo Scientific K-alpha XPS spectrometer supplied with monochromatic X-rays from an Al anode ($h\nu = \sim 1486.6$ eV). The optical bandgaps of the film were assessed by employing a UV–visible (UV–vis) absorbance spectrometer (Hitachi U3900 UV–vis spectrophotometer). The photoelectric performance of the photodetector was measured by an intensity tuned UV lamp (254 nm and 365 nm), monochromator, a program-controlled semiconductor determination system (Keithley 4200), a femtosecond pulsed laser as well as a digital oscilloscope (Tektronix TBS 1102), respectively.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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AUTHOR CONTRIBUTIONS

Q.L. and J.L. contributed equally to this work. Q.L. and J.L. conceived the project. Q.L. designed the experiments and fabricated the devices and performed the measurements with help from Ju.L. and T.-Y.L. All authors wrote the manuscript, discussed the results, and commented on the manuscript.

COMPETING INTERESTS

The authors declare no competing interests.

ADDITIONAL INFORMATION

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