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Qinglei Guo,[1] Yuting Zhao,[2] Gang Wang,[3] Da Chen,[3] Haonan Zhao,[1] Chengming Jiang,[4] Gaoshan Huang,[2] Zengfeng Di,[5] and Yongfeng Mei[2,a)]

AFFILIATIONS

[1]Center of Nanoelectronics, School of Microelectronics, Shandong University, Jinan 250100, People's Republic of China
[2]Department of Materials Science, Fudan University, Shanghai 200433, People's Republic of China
[3]Department of Microelectronic Science and Engineering, Faculty of Science, Ningbo University, Ningbo 315211, People's Republic of China
[4]Key Laboratory for Precision and Non-traditional Machining Technology of the Ministry of Education, Dalian University of Technology, Dalian 116024, People's Republic of China
[5]State Key Laboratory of Functional Materials for Informatics, Shanghai Institute of Microsystem and Information Technology, Chinese Academy of Sciences, Shanghai 200050, People's Republic of China

[a)]Author to whom correspondence should be addressed: yfm@fudan.edu.cn

ABSTRACT

This paper describes a simple and convenient approach to synthesize large amounts of ZnO nanosheets, which are suitable for producing a key component, i.e., colloidal nanoink, of printed ultraviolet photodetectors. ZnO nanosheets are produced by atomic layer deposition, where a three-dimensional polymer sponge with a large specific surface area is used as the template. Systematic studies including scanning electron microscopy, X-ray diffraction, and transmission electron microscopy reveal that the synthesized ZnO nanosheets have a good crystalline quality and mechanical flexibility. After dispersing ZnO nanosheets in a solvent to form a stable and colloidal nanoink, an ultraviolet photodetector is demonstrated through the printing method. Such a printed ultraviolet photodetector that utilizes ZnO nanosheets as the functional materials exhibits a high responsivity of ~148 A/W and a response time of 19 s. Our present study may provide a practical method to produce large amounts of functional nanosheets for printing electronics, which paves the way for developing high-performance, low-cost, large-area printed, and flexible electronics.

Ultraviolet photodetectors have attracted considerable attentions due to their wide-range applications in society, civilian, and military areas, such as ultraviolet irradiation detection, digital imaging, space exploration, missile-launch detection, and many others.[1,2] In order to realize ultraviolet photodetectors, various semiconducting nanomaterials with a wide bandgap are synthesized, including GaN,[3] SiC,[4] Ga_2O_3,[5] ZnS,[6] and ZnO.[7] Among these highly performing nanomaterials, ZnO represents a promising candidate as the absorption layer of ultraviolet photodetectors because of its unique properties, such as transparency, a wide direct bandgap (3.37 eV) at room temperature, a large excitation binding energy (60 meV), and environmental friendliness.[8] Moreover, convenient synthesis methods of ZnO nanomaterials, such as sol-gel,[9] RF magnetron sputtering,[10] pulsed laser deposition,[11] and chemical vapor deposition,[12] also offer fundamental and significant supports for creating high-performance ZnO based ultraviolet photodetectors.

With the synthesized ZnO nanomaterials, e.g., nanowires, nanotubes, and nanomembranes,[13–15] ultraviolet photodetectors can be fabricated through nano/microprocessing platforms, yet the fabrication process is complex and expensive, making them unsuitable for large-scale production. Printing electronic technology has some advantages over the traditional nano/microfabrication technology with regard to simple fabrication, large-area production, and low cost. Examples of printing electronic devices and/or systems include transistors,[16] photodetectors,[17] sensors,[18] integrated circuits,[19] and many others. To fabricate ultraviolet photodetectors utilizing the printing approach, previous studies disperse ZnO nanomaterials into a solution to form a stable and printable nanoink that can be used to print a conducting film as the absorption layer,[20] the electrical properties of which are strongly dependent on the constitution of nanoinks. For example, for nanoinks consisting of zero-dimensional (0D) nanomaterials such as nanoparticles (NPs) or quantum dots, a large number of grain boundaries will be induced in the printed continuous, conductive film. Therefore, the severe scattering from these grain boundaries will limit the electrical performances of the film.[21] Using one-dimensional (1D) nanomaterials such as nanowire, nanotube, or nanorod based nanoinks may reduce the grain boundary number in the conducting film, however, the partial surface coverage will limit the current delivery ability of the printed film.[22]

In the present study, printed, high-performance ultraviolet photodetectors are demonstrated by utilizing ZnO nanosheets as the electrical constitution of nanoinks. Synthesis of ZnO nanosheets started with growing the ZnO film on clean polyurethane (PU) sponges via atomic layer deposition (ALD). Facilitated by the perfect conformal coating of ALD, three-dimensional (3D) ZnO@PU sponges are formed after deposition. After the removal of PU through thermal annealing, ZnO nanosheets with a homogenous thickness are obtained by crashing the free-standing ZnO sponge. By dispersing the ZnO nanosheets into solvents, nanoinks suitable for both hand writing and screen printing are produced. Finally, a printed, high-performance ultraviolet photodetector with a responsivity of $\sim$148 A/W and a response time of 19 s is fabricated, suggesting a significant potential for low-cost large-area printing or flexible electronics.

Figure 1 shows the schematic diagrams for fabricating ZnO nanosheets. Here, a polyurethane (PU) sponge [see the sketched and optical images in Figs. 1(a) and 1(e)] is utilized as the template for ZnO growing by atomic layer deposition (ALD). Diethylzinc (DEZ) and water are utilized as the precursors. A 200-cycle deposition yields ultrathin ZnO nanosheets with the thickness of 34 nm. Facilitated by the intrinsic advantage of ALD technology, the deposited ZnO can conformally cover on all "skeletons" of the sponge. After the ALD of ZnO, the formed ZnO@PU sponge [Fig. 1(b)] is annealed at 700 °C for 3 h in an oxygen atmosphere, as illustrated in Fig. 1(c). Our previous studies demonstrate that three hours of annealing treatment under the above condition will completely combust the PU sponge and exhaust the gaseous reactants.[23] Therefore, only ZnO with a porous structure is left, forming a freestanding ZnO sponge, as shown in Figs. 1(d) (sketched) and 1(f) (optical image). We should stress that the PU sponge with a three-dimensional structures has a large specific surface area, which is crucial for realizing a high production of ZnO nanosheets.

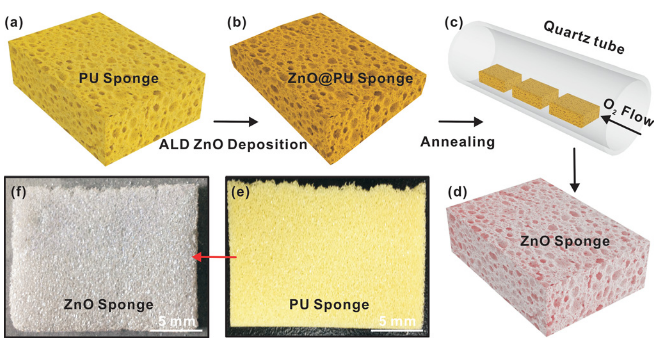

FIG. 1. Fabrication process of PU templated ZnO sponges. (a) Schematic diagram of a cleaned PU sponge as the template. (b) Sketched ZnO@PU sponge after atomic layer deposition (ALD) ZnO. (c) Annealing treatment of the as-deposited ZnO@PU sponges with a temperature of 700 °C and an O_2 flow of 0.6 l/min. (d) Schematic illustration of a three-dimensional ZnO sponge after the removal of PU. (e) Optical image of a cleaned PU sponge. (f) Optical image of a three-dimensional ZnO sponge after the removal of PU.

The frame structure of the ZnO sponge is characterized by scanning electron microscopy (SEM), as shown in Fig. 2(a). The as-obtained ZnO sponge exhibits a complex, three-dimensional, interconnected structure, which well duplicates the PU sponge template. Moreover, when the porous size is small enough (herein, less than $\sim$100 μm), ZnO can be deposited at the pore site and grows to form a joint nanomembrane, as highlighted in Fig. 2(a) with a white dashed circle. Figure 2(b) shows the SEM result of a ZnO nanomembrane, which is taken from the ZnO sponge and placed on a carbon tape substrate. Some wrinkles randomly appear, indicating a good flexibility and the ultrathin feature of the deposited ZnO. To verify the existence of ZnO in the sponge, X-ray diffraction (XRD) measurement is performed. XRD measurements of the PU sponge and ALD ZnO@PU sponge (without annealing) are also conducted for comparison. As shown in Fig. 2(c), no significant difference between the results obtained from the PU sponge and ALD ZnO@PU can be found, indicating that the as-deposited ZnO is amorphous.[24]

After the annealing treatment to remove the PU sponge, several characteristic peaks of ZnO, locating at $2\theta = 31.769°$, 34.421°, 36.252°, 47.538°, 56.602°, and 62.862° are found, which can be regarded as the (100), (002), (101), (102), (110), and (103) lattice planes of hexagonal ZnO.[25] These results suggest that the PU removal process by thermal annealing treatment improves the crystalline quality of ALD ZnO from amorphous to polycrystalline. The magnified HRTEM image is shown in Fig. 2(d); the distance between adjacent lattice fringes is assigned as $\sim$0.28 nm, which denotes the (100) planes of ZnO.[26] Moreover, the average grain size of ZnO nanosheets is about 40–50 nm. All the presented studies reveal that the sponge-templated ALD ZnO with a 3D foam structure can produce ZnO nanosheets with a good quality, which are promising candidates for printing electronics as functional materials.

Zero-dimensional nanomaterials (e.g., quantum dots and nanoparticles) and one-dimensional nanomaterials (e.g., nanowires,

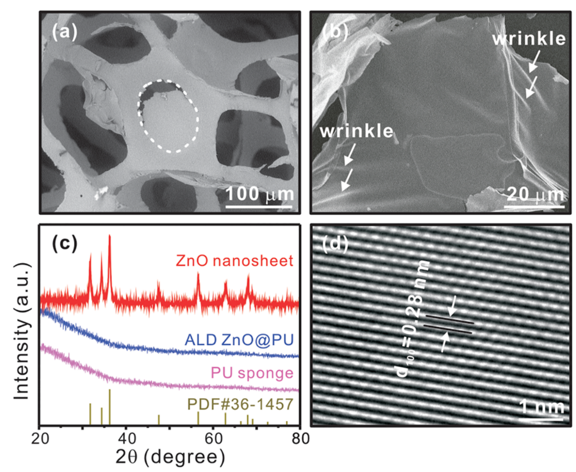

FIG. 2. Characterization of the sponge-templated ZnO. (a) SEM image of the three-dimensional ZnO sponge. (b) SEM image of a ZnO film taken from the ZnO sponge indicating a superior flexibility. (c) XRD results of the ZnO nanosheet, as deposited ZnO@PU sponge, and PU sponge. (d) HRTEM image of the ZnO nanosheet after the annealing treatment to remove PU.

nanorods, and nanotubes) have been demonstrated as good candidates for producing stable and colloidal nanoinks for printing electronics by dispersing in various solutions.[27,28] However, the large number of grain boundaries in printed films by 0D materials and the limited surface coverage of printed films by 1D materials will, therefore, strongly affect the electrical performances of the resulting films.[22] Previous studies demonstrated that using a two-dimensional (2D) nanosheet based nanoink for printing films will reduce the grain boundaries and enable a full surface coverage,[22] thus leading to high-performance electronic thin films. In this spirit, a large amount of ZnO nanosheets are produced by crashing the ZnO sponge, as shown in Fig. 3(a)-I. The obtained ZnO nanosheets are then dispersed in an ethylcellulose binder solution and terpineol to form a stable colloidal nanoink,[29] as shown in Fig. 3(a)-II.

The obtained colloidal nanoink can be applied for both handwriting and screen-printing electronics with an appropriate concentration of ZnO nanosheets. As shown in Fig. 3(a)-III, ZnO nanoinks are injected into a roller pen, and alphabets of "F" and "D" are directly written on a silicon substrate. Optical microscopy and scanning electron microscopy (SEM) images of a straight line written by a roller pen with ZnO nanoinks are shown in Figs. 3(a)-IV and 3(b), respectively. The written line is fully covered with colloidal nanoinks of ZnO nanosheets without the "coffee-ring," indicating the significant potential for serving as the electronic layer of electronic devices. To demonstrate the capabilities of ZnO nanosheet nanoinks that are utilized for creating the functional layer of electronic devices, screen-printed ZnO based ultraviolet photodetectors are fabricated. As schematically illustrated in Fig. 3(c), the construction of the photodetector consists of a printed ZnO layer, a patterned Cr/Au (5/100 nm) as the electrodes, a dielectric layer (SiO_2), and a substrate (Si) from the top to the bottom. A typical SEM image of the device is shown in Fig. 3(d) with an active area of $\sim$0.4 mm^2.

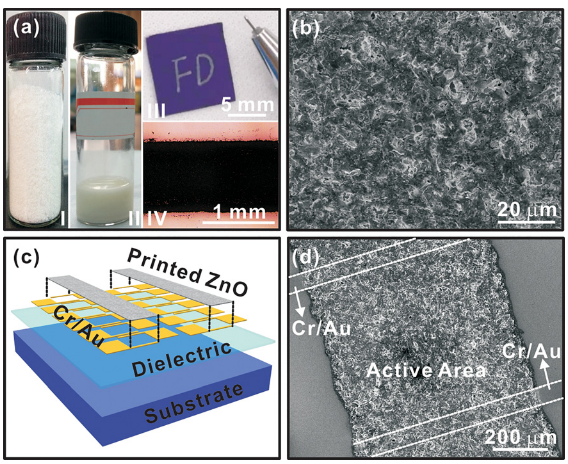

FIG. 3. Printable ZnO nanosheets for fabricating the functional electronic device. (a) Optical image of ZnO nanosheets (left) and nanoink (middle) after dispersing into the solvent. Optical image of the writable ZnO nanosheet based nanoink on the silicon substrate (top-right). Optical microscope image of a strip written by a roller pen with a ZnO nanosheet based nanoink. (b) SEM image of a strip written by a roller pen with a ZnO nanosheet based nanoink. (c) Schematic illustration of a printed ZnO nanosheet based ultraviolet photodetector. (d) SEM image of a screen-printed ZnO nanosheet based ultraviolet photodetector.

The optoelectronic properties of the printed ZnO-based ultraviolet photodetector are shown in Fig. 4(a). The inset shows an optical image of the photodetector during characterization. A power tunable light source with an emission wavelength of 365 nm is utilized to irradiate the photodetector. For the photodetector under dark condition and a fluorescent lamp illumination, no significant change in current passes through the printed ZnO film. Considering the light emitted from a fluorescent lamp mainly locates within the visible band, therefore, no photon-generated carrier will be excited in ZnO due to its wide bandgap (3.37 eV). Therefore, the current-voltage curve obtained under the fluorescent lamp illumination is similar to that obtained under the dark condition. Once the photodetector is exposed to the ultraviolet light source, the current is distinctly enhanced, which can be tuned by changing the power density of the light source, as exhibited in Fig. 4(a). More details about the photocurrent of the ZnO photodetector varying with the incident power density are shown in Fig. 4(b). At the beginning of irradiation with small power densities (e.g., 1 mW/cm^2 and 5 mW/cm^2), photocurrents of the ZnO photodetector biased at different voltages (from 1 to 10 V) rapidly increase, and this increase becomes much slower as the power density becomes larger (19 mW/cm^2) due to the saturation of the carrier traps.[30]

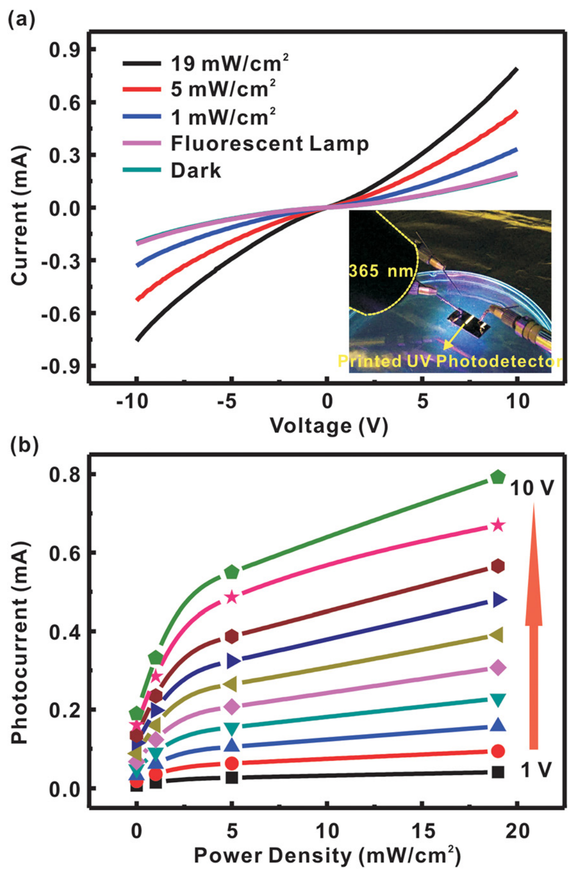

FIG. 4. Optoelectronic characterization of a screen-printed ZnO nanosheet based ultraviolet photodetector. (a) Current-voltage characteristics under different illumination conditions. (b) Photocurrent varying with the irradiated power density under different biases.

As an important figure of merit, the responsivity (R) of the printed ZnO photodetectors, defined as $R = (I_{light} - I_{dark})/P \times A$, is evaluated. I_{light} and I_{dark} denote the photocurrent and dark current, P is the power density of the illumination light, and A is the active area. As shown in Fig. 5(a), the responsivity increases with the increase in the applied voltage for all illumination situations. Notably, the responsivity reaches about 148 A/W when the applied voltage is 10 V and the power density is 1 mW/cm^2. This responsivity value evaluated from our printed ZnO nanosheet based photodetectors is much higher than that obtained from the photodetectors fabricated by single ZnO materials, such as nanosheets,[31] ZnO spheres,[32] ZnO nanoparticles (NPs),[7] and is also much higher than or comparable with that obtained from hybrid ZnO based photodetectors, such as graphene nanodots/ZnO hybrids,[33,34] Si/ZnO heterojunctions,[35] rGo/ZnO hybrids,[36] and many others,[17,37] as summarized in Fig. 5(b). Compared with the hybrid photodetectors that generally require band structure engineering, complex designs, and fabrication processes, the introduced screen-printed ZnO nanosheet based photodetector exhibits advantages that can be simply and conveniently fabricated, also capable of extending to large-scale fabrication facilitated by the screen-printing process. Figure 5(c) shows the transient optoelectronic response properties of the printed ZnO photodetector. The current of the photodetector increases rapidly with a response time (t_{rise}) of ~19 s when the light source is turned on, and drops when the light is turned off with a response time (t_{fall}) of ~48 s.

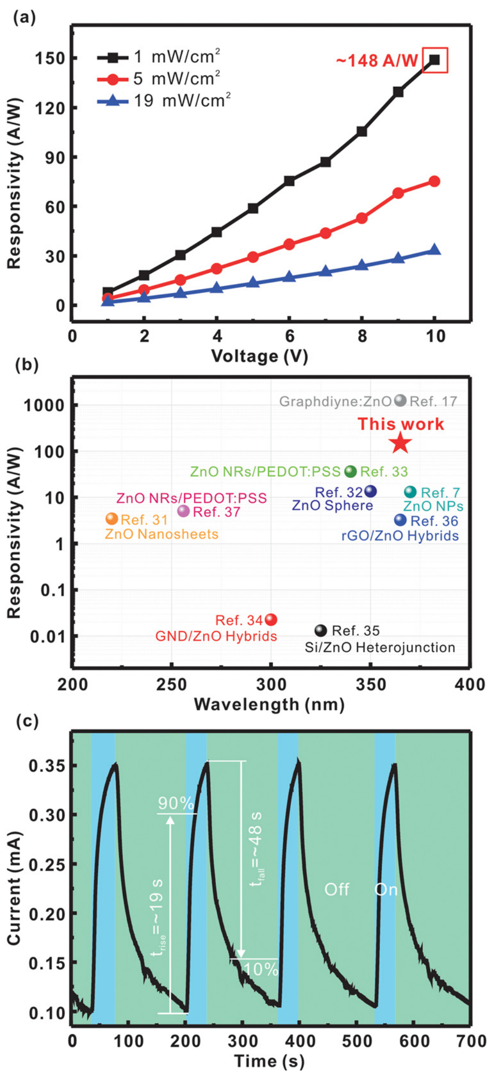

FIG. 5. Performance evaluation of the screen-printed ZnO nanosheet based ultraviolet photodetector. (a) Responsivity varying with the voltage under different irradiated power densities. (b) Summary of the responsivity obtained from various ZnO nanomaterial based ultraviolet photodetectors. The proposed ZnO nanosheet based photodetector exhibits a good responsivity of 148 A/W. (c) Current variations with a pulsed 365 nm light revealing a rise and fall time of 19 s and 48 s, respectively. The bias voltage is 5 V, and the power density of irradiated light is 19 mW/cm^2.

In summary, a simple and convenient approach that utilizes a PU sponge as the template is introduced to produce ZnO nanosheets, which are further explored as promising candidates for printing electronics. The synthesized ZnO nanosheet with an ultrathin thickness exhibits superior flexibility and good crystallinity after the annealing treatment. After dispersion into solvents to form a stable nanoink, the ZnO nanosheet is printable and writable to create a fully covered film. Utilizing this printable ZnO nanosheet nanoink, ultraviolet photodetectors are fabricated with a screen printed ZnO nanosheet film as the functional layer, where a high responsivity and fast response time are demonstrated. Our work may provide a practical, reliable, and cost-efficient strategy to synthesize large amounts of ZnO nanosheets, which are expected to be further implemented into large-area printing or flexible electronics.

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