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Fully Transparent Amorphous Ga$_2$O$_3$-Based Solar-Blind Ultraviolet Photodetector with Graphitic Carbon Electrodes

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Abstract: In recent years, transparent electrode materials have had a positive effect on improving the responsivity of photodetectors by increasing the effective illumination area of devices due to their high transmittance. In this work, by using radio frequency magnetron sputtering and simple mask technology, an amorphous Ga$_2$O$_3$-based solar-blind UV photodetector with graphitic carbon (C) electrodes was created. The device exhibits a high responsivity of 16.34 A/W, an external quantum efficiency of 7979%, and excellent detectivity of $1.19 \times 10^{13}$ Jones at room temperature under a light density of 5 $\mu$W/cm$^2$. It has been proved that C electrodes can replace the traditional noble metal electrode. Additionally, the potential of the transparent photodetector array in solar-blind imaging is explored. We believe that the present study will pave the way for the preparation of a fully transparent and high-response solar-blind ultraviolet photodetector array.

Keywords: solar-blind photodetector; graphitic carbon electrode; gallium oxide

1. Introduction

UVC generally refers to the ultraviolet electromagnetic radiation in the 100–280 nm, which does not exist on the surface of the Earth due to the thick ozone layer’s absorption as it travels through the atmosphere. Therefore, this band of light is also known as solar-blind ultraviolet light [1]. The detection of this band is called solar-blind ultraviolet detection. Solar-blind ultraviolet detection has become a research hotspot because of its low signal background noise and high detectivity. Up to now, solar-blind ultraviolet detection technology has been widely used in optical communications, ozone hole detection, high-voltage corona detection, and other fields [2–5], and it has strong research value and application prospects. As is known to all, ultra-wide band gap semiconductor materials are mainly used to prepare photosensitive layers for solar-blind ultraviolet detectors (E$_g$ > 4.5 eV), such as AlGaN [6], MgZnO [7], ZnO [8], Ga$_2$O$_3$ [9], and diamond [10]. As a new type of oxide semiconductor material with an ultra-wide band gap, Ga$_2$O$_3$ has high thermal stability [11], ultra-wide bandgap (4.5–5.2 eV), and it has natural advantages for the solar-blind ultraviolet photodetectors. Compared with other materials, it avoids complex and unstable alloying processes and is considered a natural material for building solar-blind photodetectors [12–14].

At present, solar-blind UV photodetectors based on Ga$_2$O$_3$ can be divided into heterojunction type, Schottky type, and metal-semiconductor-metal (MSM) type according to the device structure. Among them, the MSM-type photodetectors are widely used because of their low junction capacitance per unit area, simple structure, and easy integration [15]. As is well-known, non-ferrous metals with excellent conductivity and stability are generally selected as electrode materials, such as titanium, which hinder the effective absorption of incident light by devices, making MSM solar-blind photodetectors generally have the disadvantage of low responsivity. In addition, non-ferrous metals generally have high...
material costs and high technological requirements [16]. Therefore, it is very important to use low-cost, transparent electrode materials to construct solar-blind photodetectors.

Recently, Wang et al. [17] used tungsten (W) transparent electrode and GaN photosensitive layers to integrate a high detectivity solar-blind photodetector, and the average transmittance of the electrode exceeded 60% from UV light to visible light (300–750 nm). Kim et al. [18] used ruthenium oxide (RuO2) film and iridium oxide (IrO2) films as electrodes to construct a solar-blind photodetector. Compared with platinum (Pt) electrodes, the responsivity of transparent devices increased by one order of magnitude. S. Oh et al. [19] prepared β-Ga2O3 based MSM-type solar-blind photodetector using a graphene electrode with high transmittance. The device exhibits an excellent responsivity of 29.8 A/W, a preeminent light–dark current ratio of ~10⁶, an ultrahigh rejection ratio (R254 nm/R365 nm) is 9.3 × 10³, and detectivity is ~10¹² Jones. Compared with the opaque electrode, the device performance is greatly improved. Meanwhile, Wang et al. [20] showed that the performance of MSM-type solar-blind photodetector is directly related to the conductivity and transmittance of selected electrode materials. Therefore, the carbon material with high transmittance was used as the electrode of the all-transparent solar-blind ultraviolet photodetector to reduce the cost of device preparation and improve the performance of the detector.

In this work, radio frequency magnetron sputtering is used to produce an amorphous gallium oxide film without high-temperature treatment on a c-plane sapphire substrate. Then, high-transparent C-material fork finger electrodes are sputtered on the film by magnetron sputtering and a simple mask process. A fully transparent MSM-type solar-blind photodetector was successfully constructed, and the material and photoelectric properties of the device were characterized. Finally, the application of the device array in imaging is explored.

2. Materials and Methods

Material Growth and Device Fabrication. Firstly, the C-plane (0001) sapphire substrate was ultrasonically cleaned in absolute ethanol and acetone for 10 min each, then rinsed with deionized water and dried in nitrogen. Gallium oxide thin film was deposited on sapphire substrates by radio frequency magnetron sputtering using high purity gallium oxide ceramic targets (4N). The background vacuum of the chamber is 5 × 10⁻⁴ Pa, argon flow rate of 40 sccm, and the whole sputtering process lasted for 90 min at 150 W power to obtain amorphous gallium oxide material. Then, a highly transparent solar-blind ultraviolet photodetector was constructed by sputtering cross-finger electrodes on gallium oxide film by magnetron sputtering technology and mask process technology. The argon flow rate, working pressure, sputtering power, and duration were set to 40 sccm, 2.5 Pa, 100 W, and 40 min throughout the deposition process. The sputtering chamber base pressure is 8.0 × 10⁻⁴ Pa. The thickness of Ga2O3 films and carbon electrodes are about 318.73 nm and 48 nm, respectively.

Characterization. The crystal structure was analyzed by X-ray diffractometer (XRD, Bruker D8 ADVANCE A25X, Bruker AXS GmbH, Karlsruhe, Germany) with a Cu Kα line (λ = 0.1540598 nm). Raman scattering spectra were characterized by a Horiba HR Evolution spectrometer. The transmission spectra of the films and electrode materials were measured by U-4100 ultraviolet-visible spectrophotometer. The photoelectric properties of the photodetector were measured by Keithley 2450. The wavelengths are 254 nm and 365 nm light sources were provided by a 6 W ultraviolet lamp. A 500 W ultraviolet-enhanced xenon lamp was used as the source of the test system, and the spectral response of the device was tested at 10 V bias voltage. All of the experiments were run at room temperature.
3. Results and Discussion

Figure 1a shows the XRD diffraction pattern of Ga$_2$O$_3$ film. It is not difficult to see that besides the substrate peak, other Ga$_2$O$_3$-related peak positions were not observed. All of the experiments were run at room temperature, and the relevant vibration modes of the five crystal phases of Ga$_2$O$_3$ were not observed, indicating that the Ga$_2$O$_3$ thin film prepared by RF magnetron sputtering is amorphous Ga$_2$O$_3$ (a-Ga$_2$O$_3$) thin film, which is consistent with the previously reported result [21]. Figure 1c is the transmission spectrum of C electrode material and Ga$_2$O$_3$ film. Obviously, both materials have ultrahigh transmittance in the visible light region. The a-Ga$_2$O$_3$ thin film has an obvious absorption edge at about 274 nm. However, C material shows high transmittance in the whole transmission spectrum, which is more than 90%. This suggests that compared with the traditional Ti/Au electrode, the photosensitive layer of the device is more exposed to the incident light to increase the photosensitive area of the Ga$_2$O$_3$ film effectively. It is well known that the absorption spectrum can be directly converted from the transmission spectrum, and the optical bandgap and absorption coefficient of semiconductor materials satisfy the Tauc relation [22]:

$$(\alpha h\nu)^n = B \times (h\nu - E_g)$$

where $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy, $B$ is the constant, and $E_g$ is the optical bandgap. In addition, Ga$_2$O$_3$ is a direct semiconductor material for $n = 2$. Figure 1d shows the optical bandgap of gallium oxide film obtained by the Tauc formula, and obtaining the bandgap of the a-Ga$_2$O$_3$ thin film is about 4.84 eV by extrapolation.

To investigate the photoelectric characteristics of a-Ga$_2$O$_3$ thin films, the MSM-type solar-blind photodetector array ($3 \times 3$) with a C electrode was constructed by magnetron sputtering and mask process. Figure 1e shows the physical picture of the device, and it is clearly observed that the device is in a highly transparent state, which corresponds to the device possessing ultrahigh transparency in the visible light range. Figure 1f is a 3D schematic diagram of the solar-blind ultraviolet detector, in which the interfinger distance and finger width of the interfinger electrode are both 30 $\mu$m, and the finger length is 740 $\mu$m.

Figure 2a shows the I-V characteristic curve of the device under 254 nm illumination, 365 nm illumination, and dark state. An observation can be made that the photocurrent of the device and voltage manifest an evident linear relationship indicating the carbon electrodes and a-Ga$_2$O$_3$ thin film have good ohmic contact [23]. The dark current of the photodetector is around $1.64 \times 10^{-8}$ A at 10 V bias voltage. Meanwhile, the photocurrent of the device increases with an increase in light intensity because high light density promotes the generation of electron-hole pairs. To better understand the above relationship, the curve of photocurrent with light intensity under 10 V bias voltage is displayed, as shown in Figure 2b. In general, the dependence of photocurrent on light intensity can be fitted by the power function: $I = P^\theta$, where $I$ is photocurrent, $P$ is light intensity, and $\theta$ is the photocarrier activity. The value of $\theta$ obtained by fitting is about 0.54, which deviates greatly from the ideal value ($\theta = 1$). The results demonstrated that the a-Ga$_2$O$_3$ thin film has many defects, which affect the carrier transport and increase the carrier energy loss [24]. The device’s performance under different illumination was calculated to quantitatively evaluate the performance of a-Ga$_2$O$_3$ thin film-based solar-blind ultraviolet photodetectors. The photo-to-dark current ratio (PDCR) is an important parameter to measure device performance and is defined as [25]:

$$\text{PDCR} = \frac{I_{\text{photo}} - I_{\text{dark}}}{I_{\text{dark}}}$$

(2)
where $I_p$ is the photocurrent of the device and $I_d$ is the dark current. Figure 2c shows the change rule of the light–dark ratio of the device with light intensity under 10 bias voltage. It can be seen that the light–dark ratio of the device increases with the increase in light intensity. This is in accordance with the photocurrent to light intensity change rule, which is related to the increase in unit luminous flux, which promotes the generation of hole electron pairs in semiconductor materials. The photocurrent produced by the unit power of incident deep ultraviolet light on the photodetector’s effective area is what is referred to as the responsivity ($R$), which can be expressed as [26]:

$$R = \frac{I_{\text{photo}} - I_{\text{dark}}}{S \cdot P_{\lambda}}$$

where $P_{\lambda}$ is the optical power density and $S$ is the effective illumination area. The curve of $R$ with light intensity is shown in Figure 2d. An observation can be made that $R$ progressively declines as the light intensity rises, and the device’s maximum responsiveness is 16.34 A/W under the light density of 5 $\mu$W/cm$^2$. The result is owing to the energy loss caused by the increase in streamer recombination activity at high light intensity [27], which is in accord with the fitting result of the curve of photocurrent as a function of light intensity. In addition to PDCR and $R$, external quantum efficiency (EQE) and detectivity ($D^*$) are also the main performance parameters of optoelectronic devices. EQE is a parameter that measures the ability of a device to convert optical signals into electrical signals; the ratio of electron holes to incident photons determines the size of EQE, which can be expressed as [28]:

$$\text{EQE} = \frac{hcR_{\lambda}}{e\lambda}$$

where $h$ is the Planck constant, $e$ is the amount of charge, $\lambda$ is the wavelength of the incident light, and $R_{\lambda}$ is the responsivity under the irradiation of the incident light. $D^*$ represents the detection capability of the device for weak signals, which is described by the following formula [29]:

$$D^* = \frac{RS_{0.5}}{(2qI_d)^{1.5}}$$

where $S$ (0.0028 cm$^2$) is the area of effective illumination and $q$ is the amount of charge. Figure 2e,f reveals the dependence of EQE and $D^*$ on the intensity of light at 10 V bias voltage. It is conspicuous that the relationships of EQE, $D^*$, and light intensity are the same as the relationships of $R$ and light intensity, with an increase in light intensity, all of them decrease. Under the light intensity is 5 $\mu$W/cm$^2$, the EQE and $D^*$ reach the maximum value, which are 7979% and $1.19 \times 10^{13}$ Jones, respectively.

To further understand the photoelectric characteristics of a solar-blind UV detector constructed with a C electrode, the spectral response of the device at 10 V bias voltage is shown in Figure 3a. It can be seen that the responsivity of the device begins to increase from the visible band to the solar-blind band and the maximum value is at the wavelength of 275 nm. The responsivity decreases sharply with the increase in optical wavelength, and the rejection ratio ($R_{254}/R_{365}$) can reach 21.82. The device illustrates that it has a high sensitivity to solar-blind ultraviolet light, favorable solar-blind characteristics, and spectral selectivity with the result. Important quality requirements for solar-blind ultraviolet photodetectors are repeatability and stability. To test the stability of the device, the ultraviolet light source of 254 nm is controlled with a switching period of 10 s at 10 V bias voltage, and the working state of the device is collected at a light intensity of 500 $\mu$W/cm$^2$, and the transient light response curve as shown in Figure 3b is drawn. There is no obvious difference in the magnitude of photocurrent after 14 switching cycles indicating the device has good stability and high repeatability. It is well known that the light response time can be divided into rising and decaying processes, and the quantitative analysis of the time can be fitted with
the following types of exponential relaxation equations, with the functional formula as follows [30]:

\[ I = I_0 + Ae^{-t/\tau_1} + Be^{-t/\tau_2} \]  

(6)

where \( I_0 \) is the steady-state photocurrent, \( A \) and \( B \) are fitting constants, \( t \) is time, and \( \tau_1 \) and \( \tau_2 \) are two relaxation time constants corresponding to the fast response time and the slow response time of the optical response, respectively. Figure 3c shows the individual light response curves of the device at a lighting density of 500 \( \mu \)w/cm\(^2\). There is a high fitting degree of exponential relaxation equation; the rise time and decay time’s fitting outcomes are 0.10 s/1.73 s and 0.20 s/3.40 s, respectively.

Figure 1. (a) XRD diffraction pattern and (b) Raman spectra of gallium oxide films; (c) transmission spectra of the gallium oxide film and electrode materials; (d) optical bandgap of gallium oxide film form Tuac formula; (e) the original photograph of the fully transparent device; (f) the graphic views of the device.
important quality requirements for solar-blind photodetectors with different electrodes in domestic and foreign research. In general, the carbon transparent electrode can improve the performance of MSM-type Ga2O3-based solar-blind photodetectors. In Figure 2e, a physical picture of the device is shown, and it is a solar-blind photodetector array (3 × 3) with a C electrode. The device possesses ultrahigh transparency in the visible light range. Figure 2f presents a 3D schematic diagram of the device, and the optical bandgap of gallium oxide film obtained by the Tuac formula is shown in Figure 1d. The optical bandgap was obtained by extrapolation and is about 4.84 eV.

Figure 2. (a) I-V characteristic curves of a-Ga2O3 thin film-based solar-blind ultraviolet photodetector at 10 V; and plots of (b) photocurrent and fitting curve; (c) light-to-dark current ratio; (d) responsivity; (e) EQE and (f) detectivity versus light intensity.

Figure 3. (a) Spectral response at 10 V bias; (b) transient light response curve; (c) amplification of single transient light response curve and time fitting.

For better comparison, Table 1 exhibits the responsivity and photoresponse time of photodetectors with different electrodes in domestic and foreign research. In general, the solar-blind ultraviolet photodetector possesses higher responsivity and faster photoresponse time than other detectors using traditional precious electrode metals. Therefore, the carbon transparent electrode can improve the performance of MSM-type Ga2O3-based photodetectors.
solar-blind ultraviolet photodetector, and the carbon electrode has the potential to replace the traditional noble metal electrode detector.

Table 1. Comparison of main performance indexes of gallium oxide-based MSM photodetectors with different electrodes at home and abroad.

<table>
<thead>
<tr>
<th>Sample Electrodes</th>
<th>Responsivity/(A/W)</th>
<th>τ_s/s</th>
<th>τ_d/s</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Ga_2O_3 Ti/Al</td>
<td>70.26</td>
<td>0.41/2.04</td>
<td>0.02/0.35</td>
<td>[9]</td>
</tr>
<tr>
<td>a-Ga_2O_3 IZO</td>
<td>43.99</td>
<td>2.32</td>
<td>6.14</td>
<td>[31]</td>
</tr>
<tr>
<td>a-Ga_2O_3 Ni</td>
<td>138</td>
<td>0.52/3.88</td>
<td>0.32/4.00</td>
<td>[32]</td>
</tr>
<tr>
<td>β-Ga_2O_3 Ni/Au</td>
<td>0.903</td>
<td>&lt;1</td>
<td>&lt;3</td>
<td>[4]</td>
</tr>
<tr>
<td>β-Ga_2O_3 Ni/Au</td>
<td>5</td>
<td>3.3</td>
<td>0.4</td>
<td>[33]</td>
</tr>
<tr>
<td>β-Ga_2O_3 Ti/Au</td>
<td>26.1</td>
<td>7.30</td>
<td>8.05</td>
<td>[34]</td>
</tr>
<tr>
<td>a-Ga_2O_3 Ti/Au</td>
<td>5.62</td>
<td>2.68</td>
<td>5.45</td>
<td>[35]</td>
</tr>
<tr>
<td>a-Ga_2O_3 Pt</td>
<td>45.11</td>
<td>2.97 × 10^{-6}</td>
<td>148 × 10^{-6}</td>
<td>[21]</td>
</tr>
<tr>
<td>a-Ga_2O_3 Ti/Au</td>
<td>−0.4</td>
<td>0.68/6.18</td>
<td>0.49/6.93</td>
<td>[36]</td>
</tr>
<tr>
<td>a-Ga_2O_3 C</td>
<td>16.34</td>
<td>0.10/1.73</td>
<td>0.20/3.40</td>
<td>This work</td>
</tr>
</tbody>
</table>

Finally, the potential application of the device array in deep ultraviolet imaging is explored, and the principle is shown in Figure 4a. The “C” character is placed between the 254 nm lamp and the photodetector array. Ultraviolet light shines on the device through the mask, and the rest remains in the dark or weak ultraviolet light. Whereafter the current of each equipment unit is recorded unit by unit by connecting a pair of probes of the semiconductor parameter analyzer. The uniformity of the photodetector array is one of the most important requirements in imaging applications. Before the verification of imaging ability, the uniformity of the photodetector array is tested; meanwhile, record the dark current of each device unit of the device array under dark conditions and combine the results into a three-dimensional current comparison diagram, as shown in Figure 4b. As we can see, the dark current of all device units can be kept at the same level, and the narrow fluctuation indicates that the array has high uniformity possessing the potential for imaging applications. Subsequently, the application verification of solar-blind imaging was carried out. The 2D comparison diagram of the device current is shown in Figure 4c. It is worth noting that the device can display a clear “C” character shape. The above results show that the solar-blind photodetector array has the possibility to be used for solar-blind imaging and machine vision.

Figure 4. (a) Schematic diagram of the imaging system; (b) two-dimensional dark current contrast diagram; (c) two-dimensional imaging current contrast diagram.

4. Conclusions

To sum up, by using a radio frequency magnetron sputtering simple mask process, a fully transparent solar-blind photodetectors array based on a-Ga_2O_3 with the carbon electrode was created. The made device displays photoelectric performance with a considerable responsivity of 16.34 A/W, light–dark ratio of 135, the external quantum efficiency of 79.79%, and detectivity of 1.19 × 10^{13} Jones under the 254 nm light with 5 μW/cm^2. In addition, the device also shows satisfactory solar-blind characteristics and stability. It is the suggestion that the carbon electrode has the potential to replace the traditional precious metals.
metal electrode and has widespread application prospects. Finally, the possibility of the device array in solar-blind imaging is verified. This work provides a reference for the development of a fully transparent solar-blind ultraviolet photodetector with high responsivity and a thought for the industrial application of the photodetector.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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