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β-Ga_2O_3 nanoflakes/*p*-Si heterojunction self-powered photodiodes

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ABSTRACT

For the first time in the literature, a *p-n* junction photodiode based on β-Ga_2O_3 nanoflakes was fabricated on p-Si by two stage hydrothermal (nucleation and crystal growth) deposition method. The photodiode exhibited an excellent rectifying ratio of 1387 at ± 10 V. The value of responsivity to ultraviolet (UV) light was 0.16 mA/W (at 0 V) and 17.1 A/W (at -10 V), respectively. The device showed a characteristic of a self-powered device. Furthermore, this study unveiled several advantages of usage of β-Ga_2O_3 nanoflakes to boost the performance of self-powered photodiodes.

1. Introduction

Recently, low dimensional oxide semiconductors have attracted the attention of many researchers as next generation of optoelectronic devices [1,2]. Some important features including the high generation of electron and faster transport of charge carriers have made them as a potential application in the fields of solar cells, photodiodes, catalysts, gas sensors, as well as solar-blind photodetector. Among them, gallium oxide (Ga_2O_3) nanostructures have been employed in different optoelectronic applications thanks to their wide band gap, chemical and physical stability, and good luminescence properties [2]. Generally, the studies based on *p-n* heterojunction with β-Ga_2O_3/*p*-type structures have focused on deep-UV photodetector and power device applications [2]. A *p-n* heterojunction with β-Ga_2O_3/*p*-type 6H-SiC structure was fabricated for deep-UV photodiode applications [1,2]. Guo et al. reported β-Ga_2O_3/Si *p-n* heterojunctions as a solar-blind ultraviolet photodetector with a promising responsivity under 254 nm UV irradiation [3]. Moreover, n-type β-Ga_2O_3 nanobelts were also utilized for deep ultraviolet photodetection [1].

The hydrothermal growth of GaOOH onto silicon wafers was carried out by H. J. Lin and co-workers [4]. Recently, β-Ga_2O_3/GaOOH nano/microrod substrates were reported by Zhang et al. using a two-stage nucleation and crystal growth hydrothermal methods [5]. However, the optoelectrical applications and *p-n* heterojunction device performances of the homogenous/uniformed β-Ga_2O_3 arrays especially with form of nanoflakes were not investigated and stay to be realized in the literature. One of the advantages of nanoflakes is that they are interconnected with each other and create pores leading sufficiently big surface area which is desired for the devices sensitive to the light illumination. On the other hand, the synthesis of them requires relatively high temperature and long growth time, which might be considered as disadvantages of them. Herein, β-Ga_2O_3 nanoflakes/*p*-Si heterojunction device was developed for self-powered photodiode applications.

2. Experimental

At first Si(100) substrate (with 525 μm thickness and 1–20 Ω.cm resistivity) was cleaned using a standard solution (the mixture of 3:1 ratio of 96 % (H_2SO_4) and 30 % (H_2O_2)) for removal of organic contamination and then immersed in 2% hydrofluoric acid (HF) for removal of native silicon dioxide. Then, β-Ga_2O_3 nanoflakes on *p*-Si substrate was prepared by two stage (nucleation and crystal growth) hydrothermal methods according to the literature with some modifications [5]. For nucleation stage, the as-treated Si(100) substrate was immersed into a hydrothermal solution containing gallium nitrate hexahydrate (0.2 M), absolute ethanol (10 mL), and distilled de-ionized water (30 mL) and were heated at 100 °C for 1 h. Then, the crystal growth stage was carried out by a second hydrothermal solution (gallium nitrate hexahydrate (0.2 M) and DDI water (30 mL)) at 150 °C for 12 h using a Teflon-lined stainless-steel reactor. The formed GaOOH/Si substrate was washed with DDI water 3 times and then dried at 70 °C for 2 h. Finally, an annealing procedure was employed to prepare β-Ga_2O_3 nanoflakes/*p*-Si substrate at 800 °C for 4 h. As a last step, metal contacts were employed. The back electrode covers the entire back side of the device by screen-printing of Ag paste. The ohmic electrode of Ag/Al/Au was placed on the selective area of β-Ga_2O_3 nanoflakes. The

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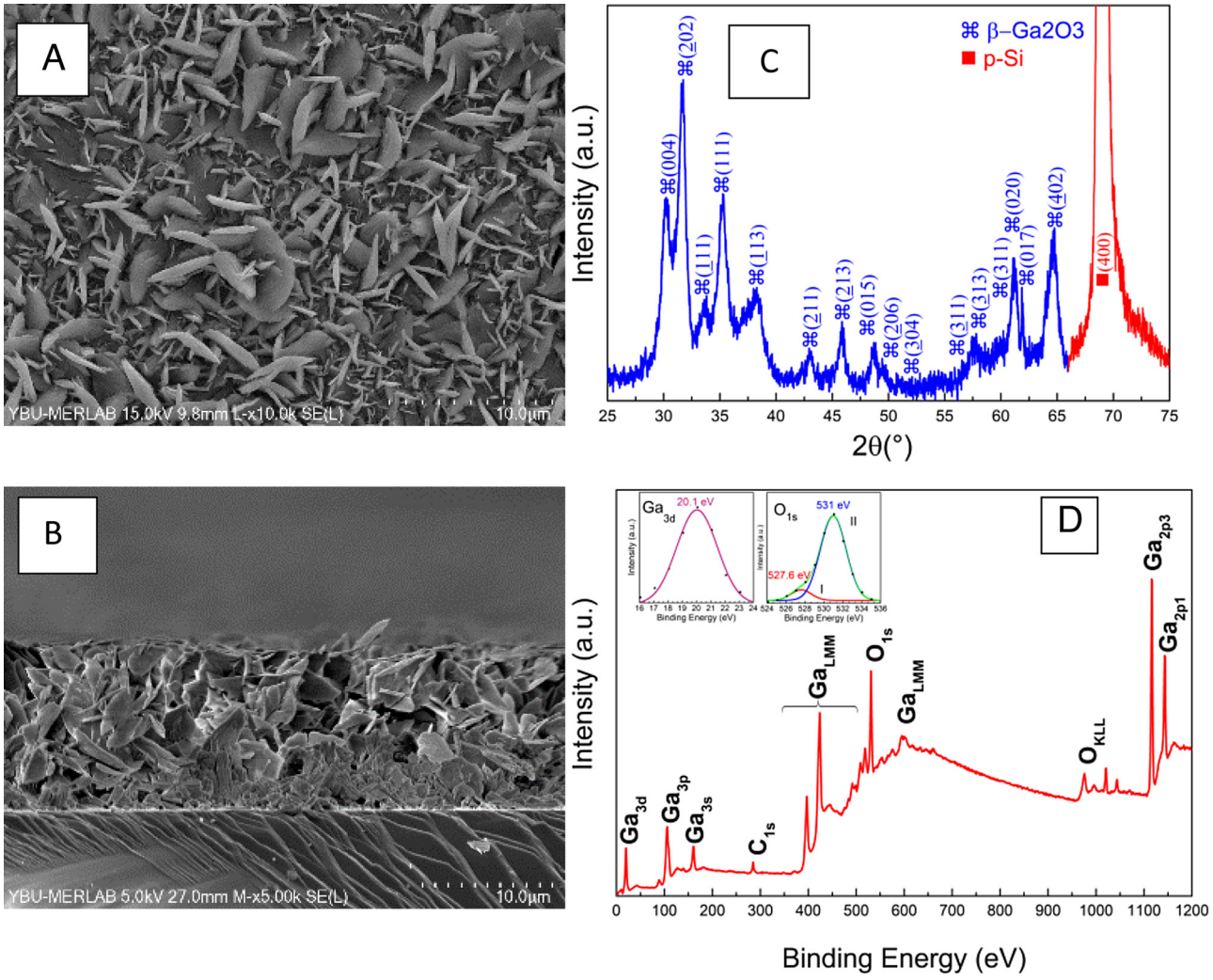


Fig. 1. (A) Top view and (B) cross-sectional view of the sample. (C) X-ray diffraction (XRD) pattern and (D) X-ray photoelectron spectroscopy (XPS) pattern of the sample.

active area of the device is 1 × 1cm^2. The current-voltage (*I–V*) characteristics of the device was measured under 254 nm UV-illumination (7 mW/cm^2 intensity) using a measurement set-up consisting of light source and Keithley 2400 source meter.

3. Results and discussion

The SEM analyses of β-Ga_2O_3 nanoflakes/*p*-Si obtained via two stage hydrothermal reaction are given in Fig. 1(A–B). As seen here, a well-grown nanoflakes of β-Ga_2O_3 were obtained in which the surface of Si(100) substrate was successfully coated with dense morphologies (Fig. 1(A)). Moreover, the clear arrangement of nanoflakes were denoted the formation of an array surface with desired distributions (Fig. 1(A)). Furthermore, the cross-sectional view of the sample was confirmed the presence of nano and micro voids/pores among the nanoflakes (Fig. 1(B)). The nanoflake structure provides some advantages over its thin film counterpart including: (1) incident light on β-Ga_2O_3 is mainly kept inside nanoflakes due to the micro-nano voids/pores that leads to an extension in optical path of the light; (2) by considering of these micro-nano voids/pores, one could also expect a large surface are occurs. Finally, the formation of these nanoflakes on Si can effectively improve the generation of electron-hole pairs (photogenerated carries) at the junction region irradiated with UV-illumination.

Fig. 1(C) represents the XRD patterns of the sample. As seen here, all of the characteristic strong peaks (i.e., (002), (111), and etc.) related to the crystalline structure of β-Ga_2O_3 were obtained with good intensities. Additionally, the major peak at (111) manifests the preferential growth of the β-Ga_2O_3 phase onto Si(100) substrate as well [5].

XPS spectra of the sample are illustrated in Fig. 1(D) and all plots are fitted well with Gaussian functions. The characteristic peaks (i.e., Ga3d, Ga2p, O1s, and etc.) for β-Ga2O3 are successfully confirmed and assigned. Fig. 1(D) illustrates that the O1s core-level peaks of β-Ga2O3 can be divided into two components, namely, I and II, which were positioned at 527.6 and 531 eV, respectively. OI corresponds to the hydroxyl groups or the adsorbed oxygen on the particle surface with the highest binding energy while the OII peak with the lowest binding energy is corresponding to the O2− state with the lowest binding energy. It could be noted that the obtained results from XPS are in good agreement with XRD.

A schematic representation of the designed device and the operation of β-Ga_2O_3 /*p*-Si heterojunction photodiode is demonstrated in Fig. 2 through a generalized energy band diagram of the device under UV illumination. Fig. 3 shows the *I–V* curves of the device under dark and illumination. The current is plotted on a semi-logarithmic scale. The results unambiguously reveal a rectifying characteristic and also demonstrate that the β-Ga_2O_3/Si heterojunction responding to UV light exhibits a photodiode behavior. Using the general diode equation [6], we determined ideality factor, barrier height and saturation current to be 6.25, 0.72 V, and 1.06 μA, respectively. Our results are consistent

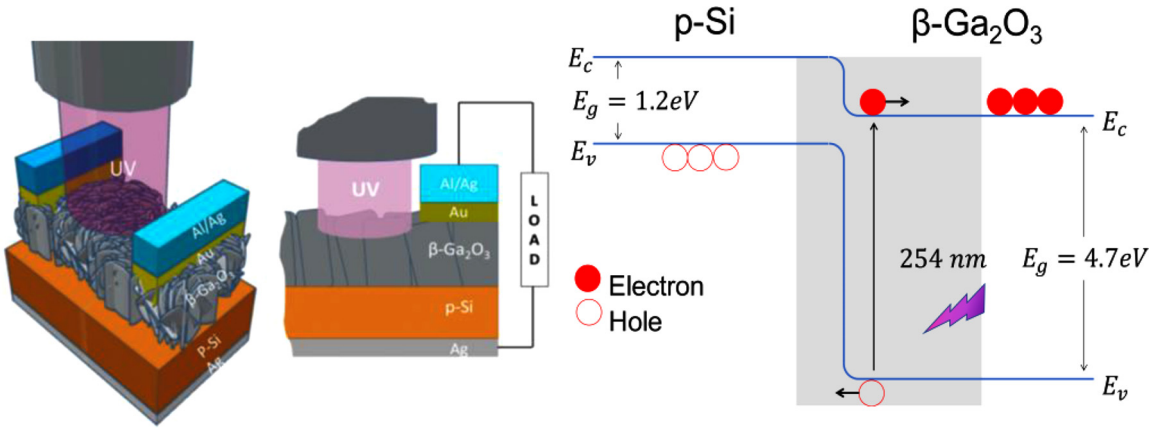


Fig. 2. (A) A schematic representation of the designed device (B) The operation of β-Ga_2O_3/*p*-Si heterojunction photodiode and generalized energy band diagram of the device under UV illumination.

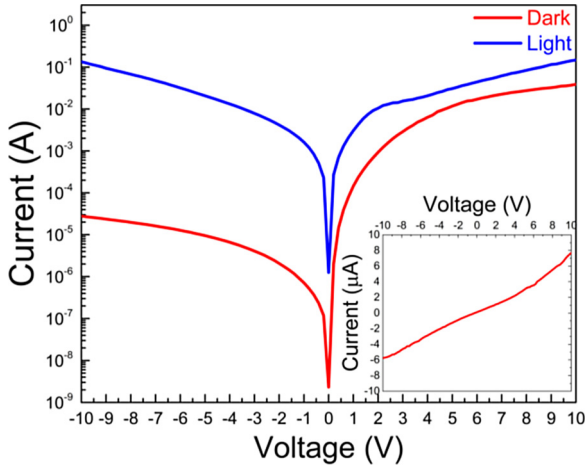


Fig. 3. The *I-V* characteristics of the device. The inset shows the *I-V* plot of ohmic contacts on β-Ga_2O_3.

with those given for β-Ga_2O_3/*p*-Si heterojunction [1]. As shown by the linear *I–V* in the inset of Fig. 3, the top metal contact is proven to form a quasi ohmic to β-Ga_2O_3. This might be due to presence of oxide vacancies as surface states on the surface of β-Ga_2O_3. It is evident that rectifying behavior of the device only arises from the heterojunction between β-Ga_2O_3 and *p*-Si. This heterojunction is responsible for the photo-response upon the light. The rectification ratio, *RR*, (i.e., the ratio (I_{FD} /I_{RD}) of the forward bias current I_{FD} to the reverse bias current I_{RD} in the dark) of 1387 at ± 10 V is estimated for the device. It is significantly higher than the reported one [7] for *p-n* diodes based on β-Ga_2O_3. While dark current is considerably low in the reverse bias region, a remarkable increase of current is observed upon the illumination in the same region. It indicates that the device is highly sensitive to UV light. The ratio of I_{RL} /I_{RD} defined as photosensitivity (*PS*) at -10 V, where I_{RL} is the reverse bias current under illumination, is obtained as 4800. The improvement in the current is attributed to a decrease in the resistance of β-Ga_2O_3 upon illumination.

Photoresponsivity (PR) of the device is defined as $PR = (I_{RLight} - I_{RDark})/Pin$, where I_{RLight} and P_{in} (=7 mW/cm^2) are the reverse current under light and incident light intensity, respectively. The value of *PR* is calculated as 17.1 A/W at −10 V, which is much larger than that of the previously reported values for the diodes based on β-Ga_2O_3 in the literature [3,8,9]. Our device with the form of nanoflakes of β-Ga_2O_3 is superior over devices with thin films or substrate of β-Ga_2O_3. The self-powered device is a device which operates without consumption of any external power. The built-in potential field occurring in the depletion region of the junction leads to separate electron-hole pairs. Then, these two carriers under this potential move in opposite directions. When the junction is held at zero external voltage, these carriers can be directed through the external circuit causing a short-circuit current. To check whether the device operates in self-powered mode without an external power source, we can also take values of the current under zero bias. Under zero bias, the dark current and the photocurrent upon illumination are estimated as 2.33 nA and 1.26 μA, respectively. Compared to thin film of Ga_2O_3, Ga_2O_3 with the nanoflakes include relatively more grain boundaries. Since grain boundaries consist of full of defects or impurities acting as carrier traps capturing free carriers, they cause changes in electrical characteristics [10–12]. In the presence of these trap regions, one can expect that the photocurrent decreases while the dark current increases [13]. Therefore, the value of dark current (2.33 nA) reported here is somewhat higher than that of the device consisting of β-Ga_2O_3 thin films (1.4 nA) [14]. On the other hand, it is still lower than that of β-Ga_2O_3 (nanobelt)/p-Si (23 nA). In our case, the remarkable difference between the dark current and the photocurrent under zero bias demonstrates zero-power consumption character of the device with a significant photoresponsivity (0.16 mA/W). Ultimately, the results imply that the device can be recognized for different optoelectronic applications.

The higher performance of the present device in terms of responsivity can be attributed to its porous structure and it might also be due to the fewer oxygen vacancies in the lattice as well [7]. To clarify why the present device provides advantages over conventional one, we should also take a look at the operation of the device upon UV light (254 nm, see Fig. 2(B)). The cut off wavelength of β-Ga_2O_3 is around 260 nm. The incident photons with 254 nm wavelength will be directly absorbed by β-Ga_2O_3 before reaching Si layer. On the other hand, to generate electron-hole pairs, the light should arrive into depletion layer locating the junction region. In this case, not only absorption coefficient of β-Ga_2O_3 (10^5 cm^{-1}) becomes important but also penetration length of incident light is needed to be taken into account. One can expect the depletion region mainly extend into β-Ga_2O_3 layer. β-Ga_2O_3 with its porous structure facilitates the reaching of the light to the depletion region and probably extends optical path of the light because of light trapping issue [15]. Once electron-hole pairs excited by the light undergo the internal electric field in the depletion region, they are separated from each other. The larger internal electric field causes an improved photocurrent in the device. Finally, they begin to transport in opposite directions and contribute to photocurrent of the device.

4. Conclusion

In conclusion, *p-n* junction photodiode behavior of β-Ga_2O_3 nanoflakes /*p*-Si heterostructures was verified. The device was considerably

sensitive to UV light due to probably the strong built-in electric field at the depletion layer. The photoresponsivity approached to 0.16 mA/W (at 0 V) and 17.1 A/W (at -10 V). The device exhibited a characteristic of a self-powered device. Ultimately, our results strongly stressed the importance of nanostructures in photodiodes, and β-Ga_2O_3 nanoflakes have a potential opportunity for the development of high-performance self-powered photodiodes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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