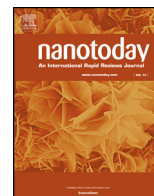




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Rapid communication

## Temperature dependence of the pyro-phototronic effect in self-powered p-Si/n-ZnO nanowires heterojuncted ultraviolet sensors

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### ABSTRACT

Self-powered pn-juncted devices fabricated with pyroelectric semiconductor have attracted much attention as active ultraviolet (UV) photodetectors (PDs), featuring with energy-efficient, active functionality and ultrafast response speed. Herein, the pyroelectric ZnO nanowires (NWs) grown on p-Si are functioned as a self-powered UV PD. Without an external voltage, the fabricated device exhibits a stable and uniform UV sensing ability with high photoresponsivity and fast response and decay time. Furthermore, the effects of ambient temperature on the self-powered UV PD are systematically investigated. Under the temperature of 77 K, the current response of the UV PD is significantly improved by over 1304%, while it is only increased by 532.6% at RT. Under the temperatures above RT, the UV PD functions well in a self-powering and stable manner even the temperature is elevated to 85 °C from RT, exhibiting good photoresponsivity of 17.0 mA/W and fast response time of 700 μs at the rise edge. By analyzing energy diagrams of the pn junction, the underlying physical mechanism of the self-powered UV PDs is carefully illustrated. This study provides guiding significance for research of high-performances UV sensing and ultrafast optoelectronic communication.

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### Introduction

Ultraviolet Photodetectors (UV PDs) have drawn considerable attention owing to their wide-range applications in industrial and scientific fields, including flame warning [1], pollutant monitoring [2,3], water purification and personal protection [4–6]. Various UV PDs featuring high responsivity, large detectivity and fast response and/or recovery speed, have been intensively investigated in the past decades based on many semiconductors with different structures (such as films, nanowires and nanoparticals) [7–12]. However, for most of the reported UV PDs, their excellent detecting performances or even normal operation relies heavily on the external power supplying [13–16]. This has long been an obstacle to meet the growing industrial requirements of UV PDs in terms of cost-saving, energy-efficiency and size minimization. Therefore, newly designed UV PDs with self-powering capability, which could

function well in a sustainable, high regularity and less maintenance manner without external power supplying, may become necessary. In the absence of external applied voltage, the intrinsic and/or self-generating electric field that can act as an effective actuating force for separation of electron-hole pairs and transportation of the charge carriers, is a critical point to fabricate a self-powered UV PDs. In addition, Silicon (Si)-based UV sensors still need to be improved in terms of the power-consumption and photoresponse performances, although Si has been the cornerstone of modern integrated circuit technology. It is of great significance to develop a low-cost and self-powered Si-based UV sensor for improving the technology of low-power monolithic-integrated system.

For pyroelectric semiconductors with non-centrosymmetric crystal structures, such as *c*-axis ZnO nanowires (NWs), the pyroelectric polarization field would be generated by time-dependently changing temperature across the semiconductors. In the case of UV detecting, the temperature of ZnO NWs would be speedily increased upon UV light illuminations, resulting in the generation of pyroelectric polarization field ( $E_{py}$ ) along *c*-axis of ZnO NWs with a distribution of pyroelectric charges at both ends of the NWs [17–19]. This light-induced pyroelectric polarization field is actually a self-generating electric field that can realize the self-powered

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functionality in ZnO NW-based devices with proper design. Moreover, the  $E_{py}$  can quickly and effectively modulate the charge transport and distribution inside the semiconductor material, readjust the energy band diagrams, and thus optimize the performance of the semiconductor optoelectronic device. This is referred to as the pyro-phototronic effect [20–24]. Considering that the temperature and its variation within ZnO NWs is the core of the induced pyroelectric polarization field, the effects of ambient temperature on the self-powered UV sensors induced by the pyro-phototronic effect is essential for improving their practical applications.

In this work, the pyroelectric ZnO NWs hydrothermally grown on p-Si substrate, are utilized to form a p-n junction for functional application as an UV PD. Without the external voltage, the fabricated device exhibits a stable and uniform UV sensing ability with high photoresponsivity and fast response and decay time. Furthermore, the effects of ambient temperature on the p-Si/n-ZnO NWs self-powered UV PD are systematically investigated under the temperatures above room temperature (RT) ranging from 25 to 85 °C and below RT ranging from 300 to 77 K. Under the temperature below RT, the current response of the UV PD is significantly improved by over 1304%, while at RT the current response is only increased by 532.6% induced by introducing the pyroelectric effect. Under the temperatures above RT, the UV PD functions well even the temperature is elevated to 85 °C from RT. And the increasing of temperature between RT to 85 °C results in, to some extent, performances declination in the UV detector. By analyzing energy diagrams of the p-Si/n-ZnO heterojunction, the working principle of pyro-phototronic effect is carefully illustrated. The relationship between the performance of the sensors and the temperature and light intensities has been studied in depth, which has guiding significance for the research of high-performances UV sensing, ultrafast optoelectronic communication, and flame/temperature monitoring. This work provides in-depth understandings about the temperature-dependence of the pyro-phototronic effect and indicates huge potential of the self-powered UV sensor in Si-based optoelectronic integration with low power consumption.

## Results and discussion

### Device structure and basic characteristics

In order to provide a precise temperature control below RT, a micro-manipulation cryogenic probe system is adopted first in this work to study pyro-phototronic effect and photoresponse performances of the UV sensor. A digital image of the micro-manipulation probe system is shown in Fig. S1 (Supporting Information). As schematically shown in Fig. 1a, the liquid nitrogen is applied as the cryostat of the system chamber, controlling the whole system temperature ranges from 300 to 77 K. By shining a 325 nm UV laser passing through the chamber window, as an optical stimulus, the pyro-phototronic effect and corresponding photoresponse performances of the p-Si/n-ZnO UV PD is comprehensively studied. Detailed structure of UV PD is graphically illustrated in Fig. 1b. The p-type Si wafer needs to be adequately cleaned firstly. Then, a method of magnetron sputtering is used to sputter a layer of ZnO seed for ZnO NWs grown by hydrothermal method [25,26]. Finally, a layer of indium-tin oxide (ITO) is deposited on the top of ZnO NWs array as a transparent top electrode and metal copper (Cu) is deposited on the back-side of Si wafer as a bottom electrode. The Ohmic contacts at Cu/p-Si and ITO/ZnO NWs interfaces were experimentally confirmed to eliminate the effect of contact resistance on the device performances. The detailed results are found in Fig. S2 (Supporting Information). Besides, the top and cross-section view of the sputtered ITO layer, shown in Fig. S2a-b, indicates that ITO was primarily deposited onto the tip of the

uniform ZnO NWs and form a suspended top ceiling layer finally, which could effectively avoid the potential short-circuit and current leakage problems. Fig. 1c1-c2 exhibit cross-section-view and top-view scanning electron microscopy (SEM) images of the grown ZnO NWs. It can be seen from the figures that the NWs are uniform with diameters of 40–70 nm and lengths of  $\sim 2 \mu\text{m}$ . Detailed description of the fabrication process and measurement method are found in the Experimental Section.

Under 325 nm laser illumination,  $I$ - $V$  characteristic curves of the self-powered p-Si/n-ZnO UV PD are measured and drawn in Fig. 1d by varying the light intensities from  $2.1 \times 10^{-6}$  to  $9.8 \times 10^{-4} \text{ W}\cdot\text{cm}^{-2}$  at 300 K, exhibiting excellent UV response and rectification characteristics at each light intensity. As well as, the output currents of the UV PD increase monotonously as increasing the light intensity, because the greater the UV intensity, the more photons are absorbed for electron-hole pairs. Fig. 1e shows the  $I$ - $t$  characteristic curves of the self-powered p-Si/n-ZnO UV PD were measured under 325 nm laser illumination through an optical chopper at 1000 Hz, reflecting a uniform and repeatable photoresponse characteristic of the UV PD. More cycles of the  $I$ - $t$  characteristic curve is shown in Fig. S3 (Supporting Information). Interestingly, the output current has a sharp rising peak, then reaches a stable value, followed by a falling edge appears, and finally reaches a constant value, which is quite different from traditional PDs.

To explore more physical insight, a single cycle of the  $I$ - $t$  characteristic curve could be divided into four distinct stages, labelled as I, II, III and IV in Fig. 1f, to detailedly explain the influence of the pyroelectric effect based on self-powered p-Si/n-ZnO UV PD. In stage 'I', at room temperature, the UV sensors maintain a steady current in the dark state that is labeled as  $I_{\text{dark}}$ . In stage 'II', when the 325 nm UV laser is suddenly irradiated, the temperature of the ZnO NWs suddenly rises induced by the photothermal property of UV light, and a pyroelectric effect is generated, in which positive polarization charge appear at the top electrode and negative polarization charge appear at the bottom electrode. By using finite volume (FV) method based on the transient heat conduction equation [20], the corresponding temperature-time curve at the moment of turning on is calculated and shown in Fig. S4 (Supporting Information), which follows the same trend with our experimental result in stage 'II'. It can be understood from the analysis that the current ( $I_{py}$ ) generated by the pyroelectric effect is consistent with the direction of the photocurrent ( $I_{ph}$ ) generated by the photovoltaic effect, hence, a sharp rising peak is generated at the moment of turning on light and the output current is labeled as  $I_{py+ph}$ . In stage 'III', when the UV light is continuously irradiated, the temperature of the ZnO NWs reaches a constant value or the temperature change amount ( $\Delta T$ ) is equal to zero, causing the pyroelectric effect to disappear rapidly. Therefore, the output current is lowered and maintained at a stable plateau, labeled as  $I_{ph}$ . In stage 'IV', at each instant of turning off the light, the temperature is lowered that causing the direction of pyroelectric polarization to be opposite to that in stage 'II', and the photovoltaic effect disappears, causing the current to drop to a negative magnitude. When the temperature gradually decreases back to room temperature, the pyroelectric effect disappears again and the output returns to dark current.

### Physical mechanisms

The physical mechanism of the pyro-phototronic effect is unambiguously elaborated in Fig. 2a-d, which corresponds to the four stages in Fig. 1f. Energy band diagram in equilibrium of p-Si/n-ZnO heterojunction is shown in Fig. 2a, indicating that the direction of the built-in electric field ( $E_b$ ) is directed to Si by ZnO. At the instant of turning on the light, the temperature of ZnO NWs suddenly rises (in the nanosecond range), which give rise to a negative pyro-polarization charges at local interface of pn heterojunction

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