**Transparent Electronics** 



# Enhancement in Performance of Transparent p-NiO/n-ZnO Heterojunction Ultrafast Self-Powered Photodetector via Pyro-Phototronic Effect

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A high-performance transparent p-NiO/n-ZnO heterojunction ultraviolet photodetector with a photovoltaic mode that exploits the pyro-phototronic effect is demonstrated. The influence of thermal treatment on ZnO films is systematically investigated, and is found to help speed up current flow due to redistribution of the pyroelectric potential within the heterojunction device. The pyrocurrent magnitude is enhanced by 1264.41% for the thermally treated device. In addition, under weak UV illumination (0.43 mW cm<sup>-2</sup>), the thermally treated device exhibits high responsivity and detectivity with respective enhancements over 5460% and 6063% compared to the pristine device. Importantly, an ultrafast response speed with rise time ≈3.92 and decay time ≈8.90 µs is achieved under self-biased conditions. The device also maintains an impressive transparency of more than 70% in the visible region. Furthermore, the basic pyro-phototronic properties of the device are thoroughly probed based on the influence of incident light intensity, externally applied bias, and change in transient switching frequencies. This work not only introduces a simple approach but also enables high-performance self-powered UV photodetection governed by the pyro-phototronic effect and demonstrated to be suitable for future transparent optoelectronic devices.

# 1. Introduction

Transparent electronics emerge as one of the most interesting and promising field of research due its wide application in the field of smart optoelectronic devices.<sup>[1]</sup> Photodetectors have set prime importance in optoelectronic devices, where the light energy is converted into electrical signal for both low light sensitivity and for harvesting energy. Based on this concept, numerous attentions have been driven to fabricate self-powered photodetectors that can work independently of external source.<sup>[2,3]</sup> Another effort is given to maintain good transparency of the self-powered photodetectors to attain high performance with wireless geometry for see-through optoelectronic devices.<sup>[4,5]</sup> Wide bandgap inorganic metal oxides are one of the preferred choices because of their excellent environmental stability with good electronic properties. Interestingly, wide bandgap materials ensure the passage of visible light making them invis-

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ible without compromising with its electronic properties. Wide bandgap materials such as zinc oxide (ZnO),<sup>[6]</sup> titanium dioxide  $(TiO_2)$ ,<sup>[7]</sup> tin oxide  $(SnO_2)$ ,<sup>[8]</sup> and nickel oxide (NiO)<sup>[9]</sup> are promising candidates for this type of applications.

In particular, "ZnO" is one of the unique semiconductor materials that can selectively detect ultraviolet light, thanks to its wide bandgap (3.37 eV) and high exciton binding energy (60 meV) at room temperature (RT).<sup>[10]</sup> Various literature reports are available on ZnO based photodetectors.  $^{\left[ 6,11,12\right] }$  In general, the performance of a photodetector depends on several factors, such as crystallinity, grain size, the presence of surface defects and proper interfacial contact. It is well established that ZnO contains surface defects, which basically act as trap centers for charge carriers.<sup>[13,14]</sup> As a result, most of the adopted ZnO synthetic routes attempt to improve the performance of the devices by morphology tuning, doping and constructing suitable junctions.<sup>[15-17]</sup> Thermal treatment is one of the efficient and simple approaches for improving optoelectronic device performance via enhanced crystallinity, grain boundary effects and reducing the defect states of the material.<sup>[18-20]</sup>



In addition to tuning of ZnO material properties using the above-mentioned techniques, recently a pyro-phototronic effect<sup>[21,22]</sup> is observed in ZnO that demonstrated to significantly enhance the photosensitivity and response speed thereby improving the photodetection performance. The existence of pyroelectric potential in ZnO is linked to its noncentrosymmetric crystal structure, which is greatly affected by temperature changes. Yang et al. have demonstrated pyroelectric ZnO for harvesting thermoelectric energy.<sup>[23]</sup> Subsequent studies have been directed toward the development of a high performance ZnO based UV photodetector that exploits the pyroelectric effect. Wang et al. reported a novel design in a ZnO/perovskite photodetector based on the pyroelectric effect for ultrafast UV sensing.<sup>[21]</sup> Recently, Peng et al. took a step forward by providing in-depth understanding of the pyro- and piezo-phototronic effects, and their role in improving the performance of self-powered ZnO based photodetectors.<sup>[22]</sup> Chen et al. have also contributed to develop a deep UV photodetector based on ZnO-Ga<sub>2</sub>O<sub>3</sub> heterojunction microwire modulated by piezo-phototronic effect.<sup>[24]</sup>

In this work, a series of transparent p-NiO/n-ZnO heterojunction UV photodetectors are fabricated and their pyro-phototronic effects are carefully investigated by varying the incident power density, externally applied bias and transient switching frequencies. To control the charge transport mechanism inside the ZnO films, rapid thermal treatments are applied to pristine ZnO



films grown at RT with 100, 300, and 500 °C, respectively. A significant improvement is observed for the p-NiO/n-ZnO device particularly with ZnO 300 °C film as compared to the pristine ZnO film where the key governing mechanism is the pyrophototronic effect coupled with the photovoltaic effect. The figures of merits, responsivity and detectivity are enhanced from 0.094 to 0.29 A W<sup>-1</sup> and  $1.2 \times 10^{11}$  to  $2.75 \times 10^{11}$  jones, respectively. Importantly, an ultrafast response speed with a rise time of 3.92 µs and fall time of 8.9 µs is achieved for the thermally treated device. Moreover, the device maintains a transparency of more than 70% in the visible region. This work thus provides an insight into the effect of thermal treatment of ZnO films on enhancing the self-induced pyroelectric effect, which ultimately results in an overall performance improvement in the p-NiO/n-ZnO based heterojunction photodetectors.

# 2. Results and Discussion

# 2.1. Schematics, Structural, Optical, and Morphological Properties

A stepwise illustration of the device fabrication procedure is presented in **Figure 1**a. At first, ZnO film is sputter deposited on well-cleaned fluorine-doped tin oxide (FTO) glass. Second, NiO is sputter deposited over the ZnO film to form



**Figure 1.** a) Schematic illustration of the device fabrication procedure, including a top view surface morphology showing the distributed Ag-NWs over NiO/ZnO. b) Energy band diagram of the p-NiO/n-ZnO heterojunction. c) Schematic illustration of the working mechanism of the self-powered photodetection with the corresponding cross-sectional field-emission scanning electron microscopy (FESEM) image. d) Absorbance and transmittance spectra of NiO/ZnO films. The inset shows the original photograph of the transparent device.



a p-n heterojunction geometry (p-NiO/n-ZnO) using a proper masking arrangement. The deposition of ZnO and NiO are conducted by following the procedure discussed in the Experimental Section. Third, high purity Ag-NWs are spin coated (3000 rpm for 60 s) onto the NiO/ZnO layer to complete the device layout. The corresponding FESEM top view morphology of the Ag-NWs distributed over the NiO/ZnO film is shown to ensure the transparency for efficient light detection. The transparent device has the configuration of Ag-NWs/NiO/ ZnO/FTO/glass with an effective area of 1 cm<sup>2</sup>. The energy level diagram with the relevant band positions of the materials constructing the photodetector is depicted in Figure 1b. The cross-sectional FESEM image of the device along with the schematic illustration of the working mechanism of self-powered photodetection present in Figure 1c. On UV illumination, excitons are generated at the interface between ZnO and NiO which are then separated by the built-in electric field induced by p-NiO/n-ZnO heterojunction. Because of the carrier selective nature of ZnO and NiO, the separated electrons will be transported through ZnO to the FTO side while the holes will be collected at the Ag-NWs through the NiO film, resulting in the formation of photocurrent in the external circuit. Figure 1d represents the absorbance and transmittance spectra of NiO/ ZnO device. Importantly a strong UV absorption is observed for the film along with a transmittance of more than 70% in the visible region.

The impacts of the thermal treatment on the structural and optical properties of ZnO film are investigated systematically. The X-ray diffraction (XRD) patterns of the ZnO films grown on FTO glass at different rapid thermal process (RTP) temperatures is presented in Figure 2a. All the major diffraction peaks show the pure and polycrystalline nature of the wurzite type structure with the space group P63mc.<sup>[25]</sup> The ZnO samples prepared at RT and 100 °C show broad diffraction peaks. Moreover, after thermal treatment at 300 and 500 °C, relatively sharp and intense diffraction peaks are observed. This reveals the improved crystallinity in the films. The Bragg positions are found to shift with increase of temperature toward a higher  $2\theta$  value, which is directly related to the decrease in lattice constant, as summarized in Table S1 (Supporting Information). The lattice parameter and crystalline size are calculated using the standard Debye-Scherrer's formula:  $\frac{1}{d_{(hkl)}^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \text{ and } D = \frac{K\lambda}{\beta \cos \theta}.$ <sup>[26]</sup> Here, D is crystalline size, *K* is shape factor ( $\approx$ 0.9),  $\lambda$  is the wavelength of X-rays

(CuK<sub> $\alpha$ </sub>), and  $\beta$  is the full width at half maximum (FWHM) in radian of the highest intensity peak, and  $\theta$  is the Bragg's angle. It is noted that the lattice constants "*a*" and "*c*" decrease with increasing temperature. This change in lattice constant can be related to the presence of defect states in ZnO. It is known that ZnO contains several types of defect states, for instance, interstitial Zinc (Zn<sub>i</sub>) and oxygen interstitial (O<sub>i</sub>).<sup>[13,14]</sup> These types of defects exist between the O<sup>2–</sup> and Zn<sup>2+</sup> layer. When the asgrown ZnO samples are thermally treated at high temperature (ZnO 300 °C and ZnO 500 °C), sufficient thermal energy is provided to position the individual atoms within suitable sites. As a result, the atoms rearrange themselves, resulting in the reduction of the lattice constants. It has been reported that the rearrangement of atoms and recrystallization enhances electron



mobility as well as electron concentration in ZnO film.<sup>[27]</sup> Therefore, enhanced performance can be expected from the thermally treated ZnO films.

Typical UV-visible absorption and transmittance spectra are recorded for the ZnO films as shown in Figure 2b. The strong UV absorption of ZnO is observed to an absorption edge of 410 nm. The optical bandgap  $(E_{\sigma})$  was calculated using Tauc's formula.<sup>[28]</sup> For the ZnO RT film, the obtained bandgap is 3.30 eV, while the ZnO 500 °C showed a reduced bandgap value of 3.25 eV (Figure S1, Supporting Information). This observation is directly related to the crystalline features of the ZnO films, where improved crystallinity is observed at higher temperatures. Lower temperatures lead to a disordered arrangement of the Zn and O atoms, because the lowest states in the conduction band become localized and thus acts as trap states.<sup>[29]</sup> These localized states will consequently shift the absorption edge to a higher energy level.<sup>[29,30]</sup> Accordingly, the low temperature processed ZnO sample has a larger energy bandgap value compared to ZnO films processed at higher temperature. Interestingly, the XRD results also support this observation, where a decrease in lattice constant is estimated at higher temperature. Therefore, the smaller the lattice constant is, the lower the bandgap. Moreover, the optical transmittance of the ZnO thin films displayed greater than 75% transparency in the visible region of the electromagnetic spectrum. However, a sharp drop in transmittance below 410 nm reflects the signature UV absorption of ZnO films. Figure 2c1-c4 shows the surface morphology of the as-grown and thermally treated ZnO films on FTO substrate. Here we observed the nanocolumnar features of ZnO.<sup>[5]</sup> When the film is heated at high temperature, the average size of the nanocolumns increases (from  $\approx 250$  to 295 nm for RT to 500 °C) and form a compact film, which is clearly observed in the case of ZnO 500 °C. This thermal treatment effectively enhances the migration capability of the atoms, resulting in more uniform and compact ZnO films. It is also expected that this will help to improve the conductivity of ZnO.

### 2.2. Photoelectrical Properties of the Transparent Device

To evaluate the photoelectrical properties of various thin films, the typical I-V curves of the p-NiO/n-ZnO heterojunction photodetectors fabricated with different RTP ZnO are presented in Figure 3a-d. A significant improvement in photocurrent is observed at higher RTP temperatures (300 and 500 °C) under UV illumination ( $\lambda$  = 365 nm) according to the absorption spectra of ZnO thin films. The insets in Figure 3 present the logarithmic I-V plots. It is found that all the photodetectors display a prominent photovoltaic effect under UV illumination. This is attributed to the charge carriers driven by the formation of a built-in electric field at p-NiO and n-ZnO interface, as presented in Figure 1b,c. In the ZnO RT photodetector (Figure 3a), the obtained open circuit voltage,  $V_{\rm OC}$  is 0.44 V and the shortcircuit current, ISC is 27.31 µA. Similarly, for the ZnO 100 °C photodetector (Figure 3b), the obtained  $V_{OC}$  is 0.43 V and  $I_{SC}$ is 25.86  $\mu$ A. However, with ZnO 300 °C (Figure 3c), the V<sub>OC</sub> is decreased to 0.28 V and  $I_{SC}$  is increased to 32.38  $\mu$ A. Again, for ZnO 500 °C (Figure 3d), the  $V_{\rm OC}$  is further reduced to 0.24 V







**Figure 2.** a) XRD pattern. b) Absorbance and transmittance spectra. c1–c4) FESEM morphologies of ZnO thin films treated at different RTP temperatures. The inset shows the size distribution of ZnO.

and  $I_{\rm SC}$  drops to 21.67 µA. The decrease in  $V_{\rm OC}$  with temperature is directly related to the rise of dark current values due to the increased thermal diffusion of the charge carriers.<sup>[31]</sup> Interestingly, similar values of  $I_{\rm SC}$  are recorded for the ZnO RT and ZnO 100 °C devices. The obtained material properties of ZnO treated at RT and 100 °C supports this result. This is expected based on the absorption measurement, which shows almost equal bandgap (3.3–3.29 eV; Figure S1, Supporting Information) for both the ZnO films (at RT and 100 °C). As a result, the energy alignments favor the collection of an almost equal number of charge carriers to the external circuit.

Further, when the ZnO thin films are treated at 300 °C, an improvement in the  $I_{SC}$  is observed. This is again attributed to the crystalline and optical properties of the films treated at high temperatures. The optical bandgap of the ZnO 300 °C

film was 3.26 eV, which improves the exciton generation and collection in the devices, resulting in an improved photocurrent. It is worth mentioning that at higher temperature, the bandgap reduction leads to the smooth transport of charge carriers through the diffusion process, rather than the recombination process.<sup>[5]</sup> However, the ZnO 500 °C sample, presents a weak photoresponse, as it behaves just like a common diode with outstanding rectification behavior. This is mainly due to the filling mechanism of the photosensitizing centers of the ZnO structures (Figure 3).<sup>[32]</sup> It should be noted that for proper photodetection, the photoactive film should have the proper bandgap, crystallinity and morphological features, as was obtained with ZnO 300 °C film. The capacity to generate photocurrent at zero bias enables the photodetector to operate in the self-powered mode, utilizing the built-in potential.







Figure 3. The *I*–V characteristics of the photodetector under dark and UV 365 nm illumination at a fixed intensity of 4 mW cm<sup>-2</sup> for a) ZnO RT, b) ZnO 100 °C, c) ZnO 300 °C, and d) ZnO 500 °C samples. The inset shows the corresponding logarithmic *I*–V plots displaying the photovoltaic effect.

### 2.3. Transient Switching Response of the Transparent Device: Pyro-Phototronic Effect

The transient responses of the photodetectors under UV illumination (4 mW cm<sup>-2</sup>) at zero bias voltage are investigated for ZnO RT, ZnO 100 °C and ZnO 300 °C, and the results are shown in Figure 4. As evidence of the photo-pyroelectric effect,<sup>[21-23]</sup> we found clear pyroelectric current peaks from the three photodetectors. The transient response of the photodetector under UV illumination can be understood based on the existence of two prominent effects, the photovoltaic effect coupled with the pyro-phototronic effect. Basically, the photovoltaic effect is based on the generation of excitons which are effectively separated due to a built-in potential at the interface between the ZnO and NiO. However, the photoinduced pyroelectric effect is associated with the development of heat across the ZnO.<sup>[21]</sup> Upon UV illumination, the generated charge carriers respond quickly to the built-in potential, the charge carriers are separated and are transported along the direction of the built-in field. Subsequently, the generated pyroelectric potential is also aligned along the direction of the photovoltaic mode and thus enhances the transient current under zero bias as evidenced by a sharp rise in current.

For the ZnO RT photodetector, an enlarged view of the single cycle transient response shows the contribution of both the photovoltaic and pyroelectric output current signal. Interestingly, it is observed that for the ZnO 300 °C photodetector, the pyroelectric current signal dominates the photovoltaic signal. The relative contributions of photovoltaic current ( $I_{ph}$ ) and pyroelectric current ( $I_{py}$ ) are estimated for the photodetectors. For ZnO RT (Figure 4a), the values of  $I_{ph}$  and  $I_{py}$  are 23.7

and 141  $\mu$ A, respectively. In the case of ZnO 100 °C (Figure 4b), almost similar values of  $I_{\rm ph}$  and  $I_{\rm py}$  are obtained, i.e., 26.73 and 145.27  $\mu$ A, respectively. For ZnO 300 °C (Figure 4c), a significant enhancement in  $I_{\rm py}$  is obtained compared to  $I_{\rm ph}$ , i.e., 35.24 and 445.58  $\mu$ A, respectively. This is consistent with the fact that higher temperature affects the distribution of pyroelectric potential within ZnO, which may speed-up the process of charge carrier separation and transport, preventing them from recombining at the interface.<sup>[21,22]</sup>

Besides this, it is noteworthy to mention that the magnitude of current enhancement,  $E = (I_{ph+py} - I_{ph})/I_{ph}$  could be determined, and a maximum value of 1264.41% is achieved for ZnO 300 °C as compared to the ZnO RT and ZnO 100 °C photodetectors (E = 594.93% and 543.47%). Importantly, it is worth noting that with the ZnO 500 °C photodetector (Figure S2, Supporting Information), the transient photoresponse did not show any pyroelectric spike under UV illumination. This result can be expected based on the material properties and I-V characteristics of the photodetector, and further demonstrates that higher temperature leads to improvement in photocurrent. Accordingly, the presence of pyroelectric current signals is negligible, and the observed photocurrent is solely due to the photovoltaic mode.

Since there are clear differences in the photodetector characteristics obtained for the ZnO RT and ZnO 300 °C, a detailed analysis of photoelectrical responses is performed for these two devices only. Additional measurements are conducted to investigate the frequency dependence of the self-powered photodetectors under UV 365 nm illumination. The corresponding transient photoresponse curves are presented in Figure S3 (Supporting Information) for different frequencies







**Figure 4.** Transient responses of the photodetector under UV 365 nm illumination at a fixed intensity of 4 mW cm<sup>-2</sup> fabricated with different RTP ZnO samples: a) ZnO RT, b) ZnO 100 °C, and c) ZnO 300 °C. The enlarged view of the corresponding single cycle transient response showing two distinct stages of the photovoltaic and pyro-phototronic currents.

from 1 to 50 Hz. Comparing the ZnO RT and ZnO 300 °C photodetectors, the output signals are clearly affected by frequency, indicating an ultrafast response (rise time, ( $\tau_r$ ) = 3.97 µs and decay time, ( $\tau_d$ ) = 13.6 µs at 50 Hz) for the ZnO 300 °C photodetector, induced by the pyroelectric effect.

It has previously been suggested that the pyroelectric effect is greatly influenced by applying external biasing.<sup>[5]</sup> Therefore, to account for this behavior, the existence of pyroelectric signals in the ZnO RT and ZnO 300 °C photodetectors is investigated under different applied bias voltages, as shown in **Figure 5**a,b. It is found that higher applied voltages (–1 V) induced larger dark current due to heating and thus reduced the pyro potential in ZnO. Again, as compared to the ZnO RT device, the pyroelectric signals for ZnO 300 °C are more prominent at low external bias (0 and –0.5 V).

Clearly, not only the pyroelectric signals are changed with external bias, but there is also a significant change in the response speed of the photodetectors. Therefore, to further confirm the relation between the ultrafast response speed and pyroelectric effect, the single cycle transient response of the ZnO 300 °C photodetector at 10 Hz under different bias voltages (0, –0.5, and –1 V) is examined, as depicted in **Figure 6**a–c. At zero bias, the calculated  $\tau_r$  and  $\tau_d$  are 3.92 and 8.90 µs, respectively. However, at –0.5 V, a quite longer response speed is recorded,  $\tau_r = 9.46$  µs and  $\tau_d = 46.64$  µs. When the bias is further increased to –1 V, the response speed is reduced significantly, to ms ( $\tau_r = 8.97$  ms and  $\tau_d = 1.74$  ms). This confirms that the prime governing phenomena behind the ultrafast response is the light-induced pyroelectric effect at lower biases.<sup>[21,23]</sup>

#### 2.4. Transparent Device Parameters and Working Mechanism

In order to offer more insight into the working mechanism of the photoinduced pyroelectric effect in the self-powered photodetector, a schematic elaborating the various stages of operation is presented in Figure 6d. The *I*–*t* curve under zero bias representing the single cycle response is divided into four specific regions. In region 1, upon UV 365 nm illumination of the ZnO, excitons are generated and become separated by the built-in field



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Figure 5. I-t characteristics of self-powered photodetectors under different external bias voltages for a) ZnO RT and b) ZnO 300 °C devices.

at the NiO/ZnO interface, followed by transport to the external circuit. In the meantime, due to UV exposure, an instantaneous rise in temperature occurs within the ZnO which results in the distribution of polarized pyroelectric charges across the device. The pyroelectric charges generally follow the direction of the photovoltaic current, which exhibits a sharp rising edge. Consequently, in region 2, the current gradually decreases and reaches a stable state while the illumination is continued, and the temperature remains constant. Because of this the pyroelectric signal disappears instantly and the photovoltaic current remains. In region 3, the UV 365 nm illumination is turned off, causing the current to drop rapidly. Simultaneously, the temperature within the system also drops, which induces the distribution of polarized pyroelectric charges in the opposite direction, leading to a sharp rise in the falling edge. Finally, in region 4, where the photodetector is kept in a dark state, the temperature falls back to room temperature and the pyro potential vanishes. Then, the current recovers to the initial dark state from the opposite pyro spike. It is worth mentioning that coupling the advantages of the pyroelectric materials is of utmost importance to configuring the ultrafast response and high photosensitivity of selfpowered photodetectors. This will certainly pave the way to the next generation of ultrafast transparent optoelectronics.<sup>[22]</sup>

The general performance of the self-powered photodetectors (ZnO RT and ZnO 300 °C) is investigated by performing intensity dependent measurements. The short circuit *I*–*t* curves for ZnO RT and ZnO 300 °C devices under different power densities of UV 365 nm illumination are presented in Figure S4a (Supporting Information) and **Figure 7**a, respectively. For both devices, the *I*–*t* curves display two stages, corresponding to the photovoltaic and pyroelectric currents under each incident power density. As already illustrated, the sharp rise in

current due to UV illumination is induced by the combined photovoltaic and pyroelectric effects, and so the corresponding short circuit current is labelled  $I_{ph+py}$ . Where the temperature remains constant and the influence of the pyroelectric current is absent, the corresponding short circuit current reaches a steady state and is labelled  $I_{ph}$ . The extracted current contribution due to both photovoltaic and pyroelectric effect is depicted in Figure 7b. A clear increase in the currents ( $I_{ph+py}$  and  $I_{ph}$ ) with the incident power density is observed, due to the fact that the amount of photocurrent generation is always proportional to the absorbed photon flux.<sup>[3,33]</sup> However, as already revealed, the  $I_{ph+py}$  has larger values compared to  $I_{ph}$  which demonstrates the enhancement provided via the pyro-phototronic effect.

In addition, the current enhancement  $(E = (I_{ph+py} - I_{ph}) / I_{ph})$ as a function of incident power density is shown in the inset (Figure 7b). It is noteworthy that the enhancement is maximum at 0.43 mW cm<sup>-2</sup> where the E value reaches 2842%. However, at higher power densities, photocurrent saturation occurs, and the enhancement remains at an almost constant value (1200–1300%). The corresponding responsivity ( $R_{\rm ph+py}$  and  $R_{\rm ph}$ ) and detectivity ( $D_{\rm ph+py}^{*}$  and  $D_{\rm ph}^{*}$ ) values under different power densities are shown in Figure 7c and Figure S5 (Supporting Information). The evolution in responsivity and detectivity is the same as that observed for the short circuit current. The maximum achieved values of responsivity are 0.29 A W<sup>-1</sup> and 5.23 mA W<sup>-1</sup> for the two distinct stages ( $R_{\rm ph+py}$  and  $R_{\rm ph}$ ) at 0.43 mW cm<sup>-2</sup>. Under the same conditions, the maximum values of detectivity are  $2.75 \times 10^{11}$  and  $4.46 \times 10^{9}$  Jones for the two stages ( $D^*_{ph+py}$  and  $D^*_{ph}$ ). These results indicate a significant enhancement in responsivity of 5460% (inset of Figure 7c) and detectivity of 6063% (Figure S5, Supporting Information) governed by the pyro-phototronic effect. In a comparison of the





**Figure 6.** *I–t* characteristics of the self-powered photodetector for the (Ag-NWs/NiO/ZnO 300 °C/FTO-glass) device, showing the single cycle response at different external bias voltages: a) 0 V, b) -0.5 V, and c) -1 V. d) Transient single cycle response of the photodetector at zero bias illustrating the working mechanism of the pyroelectric effect coupled with photoexcitation processes segmented into four regions (± are the pyroelectric charge distribution).



**Figure 7.** a) *I–t* characteristics of the self-powered photodetector for the ZnO 300 °C device under UV 365 nm illumination with different incident power densities from 0.15 to 4 mW cm<sup>-2</sup>. The inset presents an enlarged view of the *I–t* curves under corresponding illuminations. b) The short-circuit current response and c) the responsivity (*R*) response showing the photovoltaic contribution combined with the pyroelectric current at different UV intensities. The insets of (b) and (c) show the enhancement of  $I (E = (I_{ph+py} - I_{ph}) / I_{ph})$  and  $R (E = (R_{ph+py} - R_{ph}) / R_{ph})$ .

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<b>1</b>	Table 1.	Performance	comparison of	self-powered ZnO-	based heterojunction	UV photodetector	governed by pyro-phototronic effect.
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Device	P [W cm <sup>-2</sup> ]	$R_{\lambda}$ [A W <sup>-1</sup> ]	D* [Jones]	<i>τ</i> <sub>r</sub> [s]	$ au_{d}$ [s]	λ [nm]	Ref.
NiO/ZnO	12.1 µ	0.19	$3.8  imes 10^{12}$	323 m	12 m	370	[34]
NiO/ZnO	3 m	20 µ	$7.2 \times 10^{11}$	41 μ	71 μ	365	[35]
V <sub>2</sub> O <sub>5</sub> /ZnO	4 m	36.34 m	$6.04\times10^{14}$	4 μ	16 μ	365	[36]
Cl-ZnO/PEDOT: PSS	0.3 m	2.33 m	$1.54  imes 10^{10}$	28 m	23 m	365	[37]
Cu <sub>4</sub> O <sub>3</sub> /ZnO/ITO	-	-	_	33 m	89 m	365	[38]
ZnO/CuSCN	6 m	0.0075	_	4 n	6.7 μ	380	[39]
ZnO/perovskite	19 μ	26.7 m	$4.0  imes 10^{10}$	53 μ	63 µ	325	[21]
ZnO/PEDOT: PSS	2.3 m	3.5 m	$7.5 imes10^9$	5.8 m	7.3 m	325	[22]
NiO/ZnO	0.43 m	0.29	$2.75  imes 10^{11}$	3.92 μ	8.9 μ	365	This work

ZnO RT (Figure S4c,d, Supporting Information) and ZnO 300 °C photodetectors, a significant improvement in the responsivity values (from 0.094 to 0.29 A W<sup>-1</sup>) is observed, confirming the key governing principal to be the pyro-phototronic effect via the thermal process. Considering all the merits of the photodetectors, i.e., responsivity, detectivity, and response speed, a comparison list with all the reported pyroelectric-induced self-powered photodetectors is summarized in **Table 1**.<sup>[21,22,34–39]</sup>

It is worth mentioning that because of the thermal treatment of ZnO, this study reports the best performance based on the photoinduced pyroelectric effect coupled with the photovoltaic effect. Notably, for practical applications, it is necessary to properly balance all of the critical photodetector parameters. In this study, the proper balance in the ZnO 300 °C photodetector is reflected in the responsivity, detectivity, and response speed values, demonstrating the potential of the pyroelectric influence, following the thermal treatment of ZnO.

# 3. Conclusion

In summary, a self-powered transparent UV photodetector based on p-NiO/n-ZnO heterojunction is demonstrated where both the photovoltaic and pyro-phototronic effects are combined to significantly enhance the performance. Specifically, thermal treatments are performed on pristine ZnO films at 100, 300, and 500 °C, respectively. The thermal treatment on ZnO acts to distribute that pyroelectric potential and provide an alternate effective route for current transport in the device. It is demonstrated that the photovoltaic effect coupled with the pyro-phototronic effect induced by UV illumination enhances the overall performance of the photodetector, resulting in high responsivity (0.29 A  $W^{-1}$ ), high detectivity ( $2.75 \times 10^{11}$  jones), and ultrafast response speed (3.92/8.9 µs). It is concluded that this study presents a simple and fast approach using thermal treatment to construct a transparent ultrafast self-powered UV photodetector, where the prime governing mechanism is the pyro-phototronic effect.

contact electrode. Commercially available FTO-coated glasses were used as the conductive substrate, while FTO film served as the bottom transparent electrode. Argon (Ar) (99.9% pure) and oxygen (O<sub>2</sub>) (99.9% pure) gases were introduced as the carrier gas and reactive gas for the sputtering process. Organic solvents such as ethanol and acetone were used with deionized water for all cleaning purposes.

Deposition Procedure: The experiment was carried out in a cosputtering system (SNTEK Korea). FTO glasses were used as the substrates to prepare the photodetector. Initially, the FTO glass substrates were cleaned with acetone, ethanol, and deionized water in an ultrasonic bath for 10 min each, followed by drying in the presence of nitrogen gas. The cleaned FTO glass substrates were then placed inside the cosputtering system. A ZnO target was mounted in a planar magnetron assembly for sputtering. Prior to film deposition, the system was evacuated down to a base pressure of  $\approx 5 \times 10^{-5}$  Torr. After that, Ar gas (50 sccm) was flowed into the system to maintain a working pressure of  $5 \times 10^{-3}$  Torr. The sputtering of ZnO is initiated by applying RF power of 300 W to the magnetron gun. The pristine ZnO films are sputtered at room temperature. The deposited time was fixed at 60 min and the sputtering substrate was rotated at 5 rpm. The as-deposited ZnO thin films were then thermally treated at different temperatures (RT, 100, 300, 500 °C) by the RTP system. During the RTP process, the target temperature was applied for 10 min under vacuum ( $2 \times 10^{-2}$  Torr). The resulting samples were designated: ZnO RT, ZnO 100 °C, ZnO 300 °C, and ZnO 500 °C, respectively.

After the RTP process, the ZnO samples were loaded inside the cosputtering system again for the deposition of nickel oxide (NiO).  $O_2$  reactive gas was flowed with Ar (sputtering gas) at a ratio of 1:4 to form a NiO film from the pure Ni sputtering at DC 80 W. The NiO formation was performed for 15 min.

*Characterizations*: The structural characterization of the thin films was obtained using XRD (Rigaku Smartlab). Optical measurements were made using a Shimadzu-made (UV-2600) UV-vis spectrophotometer. The planar morphology of the thin films was investigated by FESEM (JEOL, JSM 7800F). The electrical characterization and photoresponse were measured under an UV light-emitting diode source (365 ± 10 nm). To investigate the photoresponse of the transparent device (Ag-NWs/NiO/ZnO/FTO), the chronoamperometry method was used, with pulsed light illumination and varying light intensity. The UV pulse was generated by a function generator (MFG-3013A, MCH Instruments). The intensity of UV light was calibrated using a power meter (KUSAM-MECO, KM-SPM-11).

## 4. Experimental Section

Materials: A ZnO target (99.99% purity, dia. 4 in.) and Nickel (Ni) target (99.99% purity, dia. 4 in.) were used for sputtering. Ag NWs (99.99%) graded reagent was used as a precursor for preparing the

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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# **Conflict of Interest**

The authors declare no conflict of interest.

# **Keywords**

p-NiO/n-ZnO, pyro-phototronic effect, transparent electronics, ultrafast photodetectors

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