

# Performance Enhancement of Hydrothermally Grown ZnO Based Ultraviolet Photodetector Using Wafer Transfer and Pyramidal Surface Textures

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## Abstract:

The use of substrate transfer for the fabrication of vertical ultraviolet photodetectors (UV-PDs) based on hydrothermally grown (HTG) n-ZnO/sputtered p-CuO heterojunction (HJ) is demonstrated. As compared with that of the conventional device without wafer transfer, improvements in UV light responsivity (defined as the ratio of current density under UV 365 nm light irradiation to that of in dark) from 29 to 310 is obtained, which is attributed to the vertical structure enable a much shorter conduction path and make possible the removal of amorphous seed layer. With a further chemical etching to HTG ZnO layer after wafer transfer, pyramidal surface textures were formed and UV light response as high as 943 was obtained. The additional gain in photo responsivity is due to a reduced light reflection and the removal of highly-defected initial ZnO growth layer.

## 1. Introduction

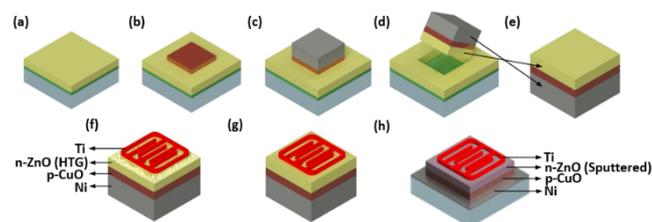
ZnO is a thermally stable n-type hexagonal wurtzite structure semiconductor with a direct wide band gap of 3.37 eV and excellent optoelectronic properties.<sup>1-3</sup> With many advantages over other semiconductors as a photodetector material, ultraviolet photodetectors (UV-PDs) based on ZnO-based heterojunctions (HJs) with alternative p-type materials such as CuO, CdS, and NiO have been reported in recent years.<sup>4-7</sup> In essential, film type HJ is more favorable to device applications for having a much larger junction area than those of using nanostructures. Especially, high-quality ZnO film and heterostructure are vital for fabricating high performance UV PDS. For the synthesis of ZnO film on lattice mismatched substrates with facile hydrothermal growth (HTG) method, a ZnO-based amorphous seed layer is usually required to provide nucleation sites to initiate ZnO growth. However, both the seed layer and the initial growth ZnO layer usually have high density of dislocations and defects, which deteriorates its photoelectric properties and limits device applications. In this study, to improve the quality of HTG-ZnO film and avoid the adverse impacts of the initial growth layer, seed layer, and high series resistance encountered in common lateral-structured ZnO-based HJ-PDs, vertical structured HTG-n-ZnO/p-CuO UV-PDs were fabricated on sapphire substrate through a simple substrate transfer technique using sonicating bath process. In addition, a chemical etching to remove the highly-defected ZnO initial growth layer and the seed layer is also employed. It is found that pyramidal textures formed on the HTG-ZnO film after etching increases considerably photo responsivity of UV-PDs. Effectiveness of the removal of seed layer and defective initial ZnO growth layer on UV-PDs performance is investigated. A comparative study on the performance vertical structured UV-PDs with and without wafer transfer is also made and discussed.

## 2. Experimental

The key fabrication processes of vertical structured p-CuO/HTG-n-ZnO UV-PDs are schematically shown in Fig. 1. Sapphire substrates were used. First, a 100-nm-thick ZnO seed layer was deposited on the sapphire substrate using radio frequency (RF) sputtering and a 800-nm-thick ZnO

film was synthesized by hydrothermal method using a solution with 0.07 M zinc nitrate hexahydrate ( $Zn(NO_3)_2 \cdot 6H_2O$ ) and hexamethylenetetramine ( $C_6H_{12}N_4$ ) at 60°C for 15 h (Fig. 1 (a)). Then a 300-nm p-CuO was deposited and patterned on the HTG-ZnO layer by RF sputtering to form p-CuO/n-ZnO HJ structure (Fig. 1(b)). To form a metal substrate to support device structure after wafer transfer, a 200-nm-thick patterned Ni electrode was deposited on the p-CuO layer by electron beam (e-beam) evaporation, followed by a 55- $\mu$ m-thick Ni electroplating (Fig. 1(c)). Then the p-CuO/n-ZnO HJ structure was lifted off from sapphire substrate using a sonicating bath process (Fig. 1(d)). Figure 1(e) shows the HTG-n-ZnO/p-CuO HJ with a Ni substrate, which is illustrated by turning upside down the detached structure shown in Fig. 1(d). Note that part of samples were subjected to a chemical etching using 2 M HCl for 5 s to remove the highly-defected ZnO initial growth layer and form pyramidal surface textures on the top of ZnO film to reduce UV-light reflection. Finally, a 200-nm-thick Ti electrode was deposited on the n-ZnO layer by e-beam evaporation to serve as cathode electrode. Figs 1(f) and 1(g) show the schematic device structures with and without chemical etching, which are referred to as sample A and B, respectively. For comparison, p-CuO/n-ZnO HJ-PDs with the layer structure all deposited by RF sputtering on sapphire substrate (called sample C) were also prepared (Fig. 1(h)).

Fig. 1 (a)-(e) Key fabrication process flow of the vertical structure HTG-



ZnO-based UV-PDs via wafer transfer and surface textured etching. (f) Sample A, (g) sample B, and (h) sample C.

Note that the active region of all prepared PDs is with the same size of 1 mm $\times$ 1 mm. Current-voltage (I-V) characteristics and photo responses were carried out on a Keithley 2430 source meter. And UV 365 nm light with a power density of 3 mW/cm<sup>2</sup> was used for photo sensing measurements.

## 3. Results and discussion

Figure 2 shows Transmission electron microscopy (TEM) image and X-ray diffraction (XRD) pattern of HTG-ZnO. Lattice images and selected area electron diffraction (SAED) of the HTG-ZnO film are shown in Fig. 3(b) and 3(c), respectively. Note that the lattice spacing of 0.26 and 0.16 nm correspond well to the (0002) and (1120) planes, respectively. Together with the diffraction peak that corresponds to the (0002) plane shown in Fig. 3(d), it suggests that the HTG-ZnO has a hexagonal wurtzite structure and might have crystalline structure according to the standard JCPDS card No. 36-1451. Fig. 3(e) shows the TEM image of sample A. It reveals the layer

structure of electroplated HTG-ZnO/sputtered-CuO/Ni structure, indicating that the success of transfer technique and suitability for device processing.

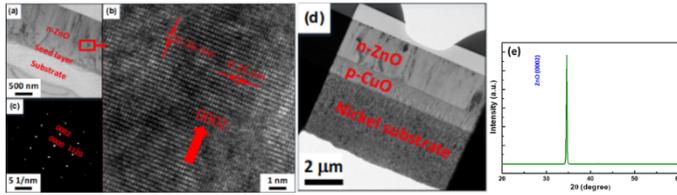


Fig. 2 Material characterization for the HTG-ZnO film. (a) TEM image, (b) Lattice images, (c) SAED pattern, (d) TEM image and (e) XRD pattern of sample A.

Figure 3 shows the SEM images of the HTG-ZnO film as grown, after wafer transfer, and after HCl etching. Note that a highly-defected initial ZnO growth layer exists atop on the amorphous ZnO seed layer (the region at the bottom of Fig. 3(a)), which could deteriorate the optoelectronic behaviors of PDs. A sonication process which exerts a mechanical stress to detach HTG-ZnO film from the fragile amorphous ZnO seed layer (Fig. 3(b)). Figure 3(c) shows the surface morphology of the detached HTG-ZnO film after chemical etching to remove the highly-defected initial ZnO growth layer. Pyramidal textures were obtained on the surface of the transferred HTG-ZnO film, suggesting that the HTG-ZnO film is with a crystalline structure. An enhanced light absorption can be expected.

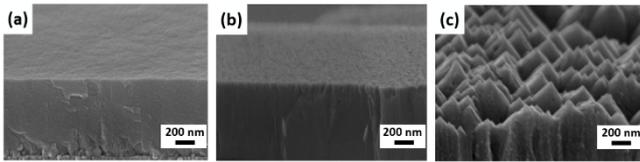


Fig. 3 SEM images of HTG ZnO films. (a) As grown and (b) after wafer transfer. (c) surface morphology of HTG ZnO after wafer transfer after HCl etching.

Figure 4 shows a comparison of the experimental J-V characteristics of the three types of HTG-ZnO based HJ-PDs in dark ( $J_{\text{Dark}}$ ) and under UV 365 nm light ( $3 \text{ mW/cm}^2$ ). All devices show good rectification behaviors. Note that sample A has the lowest reverse dark current, the highest forward current, and the highest photo current under UV light irradiation as expected.

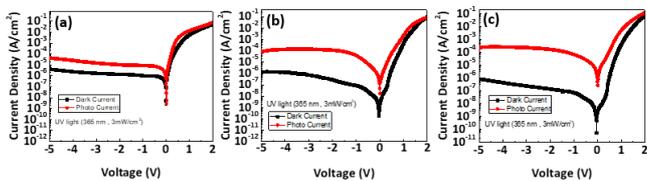


Fig. 4 The J-V characteristics of HTG-ZnO based HJ-PDs. (a) Sample A, (b) Sample B, and (c) Sample C.

Figure 5 shows the waveforms of photo current  $J_{\text{UV}}$  of the three types PDs. Table 1 summaries the quantitative details of the measured photo responsivity (defined as the current ratio of  $J_{\text{UV}}/J_{\text{Dark}}$  at  $-1 \text{ V}$ ) and photo current waveforms. The photo responsivity/rise time/fall time of sample C, B, and A are about 29/34 s/23 s, 310/18 s/6 s, and 943/12 s/2 s, respectively. As compared with Sample C, in addition to the profound increase in response speed, it indicates that  $310 \times$  increase in photo responsivity is achieved by Sample B through wafer transfer to get rid of seed layer and the formation of vertical HJ-PD structure. It is attributed to sample B has a much lower series resistance arising from the vertical configuration and

getting rid of the amorphous seed layer. In addition, the removal of the highly-defected ZnO initial growth layer and the formation of pyramidal textures on the HTG-ZnO surface in Sample A bring another gain of about  $943 \times$  in photo responsivity. Our experimental results confirms that the wafer transfer which makes possible the removal of amorphous seed layer and surface chemical etching which removes the highly-defected initial ZnO growth layer are very beneficial to the enhancement of HTG-ZnO based UV-PDs.

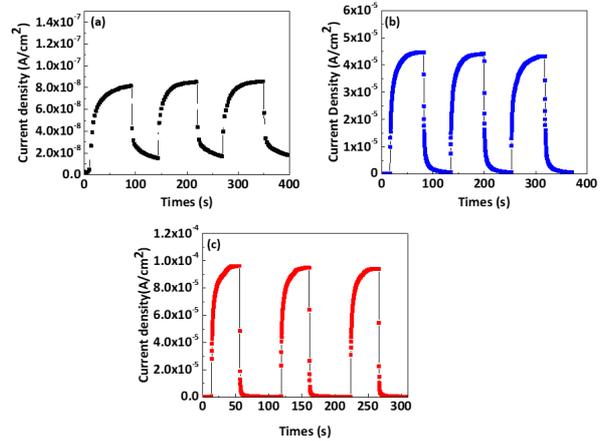


Fig. 5 Waveforms of photo current of the three types of ZnO-based HJ-PDs. (a) Sample C, (b) Sample B, and (c) Sample A.

Table.1 Comparison of photo responsivity of HTG-ZnO based HJ-PDs prepared in this work.

	Response	$J_{\text{UV}}$ ( $\text{A/cm}^2$ )	$J_{\text{Dark}}$ ( $\text{A/cm}^2$ )	Rise time (s)	Fall time (s)
p-CuO/sputtering-n-ZnO	29	$8.16 \times 10^{-6}$	$2.8 \times 10^{-7}$	34	23
p-CuO/HTG-n-ZnO	310	$4.46 \times 10^{-5}$	$1.44 \times 10^{-7}$	18	6
p-CuO/HTG(etched)-n-ZnO	943	$9.62 \times 10^{-5}$	$1.02 \times 10^{-7}$	12	2

#### 4. Conclusion

The use of substrate transfer for the fabrication of vertical UV-PDs based on sputtered-CuO/HTG-ZnO HJ have been demonstrated. Experimental results have revealed that use of wafer transfer via sonication bath process makes possible the removal of highly-defective ZnO initial growth region and formation of pyramidal surface textures, which play crucial roles in improving photo responsivity of vertical structured p-sputtered-CuO/HTG-ZnO HJ-PDS. Though further optimization for device processing is still needed, a photo responsivity as high as 943 with acceptable rise/fall time of 12 s/2 s suggests the proposed sputtered-CuO/HTG-ZnO HJ-PDs could be a very promising candidate for environment UV light detection.

#### Acknowledgements

This work was supported by the Ministry of Science and Technology (MOST), Taiwan, under contract No. MOST 104-2221-E-006-130-MY3, and MOST 105-2221-E-006-196-MY3

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