Research Article

Oxidized Nano-Porous-Silicon Buffer Layers for Suppressing the Visible Photoresponsivity of ZnO Ultraviolet Photodetectors on Si Substrates

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This paper demonstrated the fabrication and optoelectronic characteristics of ZnO ultraviolet (UV) photodetectors fabricated on Si substrates with oxidized nano-porous-Si (ONPS) buffer layers. ONPS layers were prepared on the surfaces of Si substrates by use of an electrochemical anodization technique following a rapid-thermal-oxidation process. Experimental results indicated that application of ONPS buffer layers not only improved the crystallinity of the deposited ZnO thin films but also greatly restricted the visible-to-infrared photoresponse that was generated from the light absorption of Si substrates. The developed ZnO-on-ONPS photodiodes achieved high photoresponsivity for the incident UV light of 300 ~ 400 nm and got a large photo-to-dark current ratio up to 104 at wavelength of 375 nm under a bias of 5 V. Therefore, ZnO on ONPS provides a highly potential approach for the development of low-cost visible-blind UV photodetectors.

1. Introduction

Ultraviolet (UV) photodetectors are important devices due to their various applications including ozone layer monitoring, solar astronomy, missile plume detection, space communications, fire alarm, and combustion monitoring [1, 2]. Of particular value are visible-blind and solar-blind UV detectors, whose low sensitivity for visible and infrared (IR) light can ensure accurate measurement in the UV with minimal background. At present, commercial solid-state UV photodetectors still mostly use Si-based optical devices. Nevertheless, these devices are sensitive to visible and infrared radiation and have small responsivity in UV regions because of the low bandgap energy of Si. Current researches on visible-blind UV photodetectors mainly concentrated on the III-nitride materials [3, 4]. However, epitaxial processing of III-nitride thin films is quite difficult and is not compatible with the Si integrated circuit process. Therefore, it is not easy to reduce the cost of related products for commercial applications.

As a wide- and direct-bandgap semiconductor material, zinc oxide (ZnO) has been considered a promising candidate for UV detecting applications [5, 6]. But, it is difficult

to obtain high-quality ZnO films directly growing on Si substrates due to the large differences in the lattice constant and the thermal expansion coefficient between ZnO and Si. Hence, the applications of ZnO-on-Si devices were limited.

In recent year, owing to the low price and ready availability of Si substrates as well as the compatibility with Si integrated-circuit fabrication process, hetero growth of ZnO films on porous Si (PS) has become an important method for the development of novel devices [7–10]. Many studies pointed out that the special sponge-like structures of PS can assist nucleation reaction and reduce the stress in the hetero-epitaxial films. Some materials grown on PS got better film crystallinity and film quality than those grown directly on silicon substrates [11–13]. Furthermore, preparation process of PS from Si wafers is quite simple by using an electrochemical anodization technique. Therefore, the combination of ZnO and PS is very potential for development of low-cost UV photodetectors [14, 15]. Unfortunately, ZnO-on-PS UV photodetectors are still not visible-blind because PS materials are sensitive to visible and IR radiation.

In this work, ZnO UV photodetectors with highly restricted photoresponsivity to visible and IR light were

FIGURE 1: Schematic device structure of the ZnO photodiode fabricated on a Si substrate with an oxidized nano-porous-Si (ONPS) buffer layer.

fabricated on Si substrates by introducing oxidized nano-porous-Si (ONPS) as the buffer layers.

2. Materials and Methods

Heavily doped ($3\sim5\text{ m}\Omega\text{-cm}$) p^+ -type (100) Si wafers were used as the starting substrates. After a standard RCA cleaning process, nano-porous-Si (NPS) layers were prepared on Si substrates by an electrochemically anodic etching technique. The anodization was carried out in an etching solution with concentration ratio of $\text{HF}:\text{ethanol}:\text{H}_2\text{O} = 3:1:1$, under etching current density of 10 mA/cm^2 . Then, NPS layers were transformed into ONPS layers through a rapid-thermal-oxidation (RTO) process. According to Lee et al. [16], the photoconductance of an oxidized PS layer increased with the oxidation time (t_{ox}) or oxidation temperature (T_{ox}) to a maximum value and then reduced for higher t_{ox} or T_{ox} . To obtain high photoresponsivity of devices, a t_{ox} of 60 s and a T_{ox} of 800°C were employed in the RTO process based on the empirical results of experiments. After the formation of ONPS buffer layers, ZnO thin films were deposited on the samples by sputtering under RF power of 100 W and Ar pressure of 12.6 mTorr at room temperature. The samples were then annealed under different temperatures in N_2 ambient to improve the crystallinity of ZnO films. Finally, aluminum (Al) interdigitated electrodes were deposited on the top of the samples by an e-beam evaporator to complete the device structure of a metal-semiconductor-metal (MSM) photodiode, as shown in Figure 1. The structure of the developed ZnO UV photodiode contained, from top to bottom, 500 nm Al interdigitated electrodes, a 100 nm ZnO film, a $3.5\text{ }\mu\text{m}$ ONPS layer, and a 300 mm p-Si substrate.

The morphology of ZnO films and ONPS layers was observed by field-emission scanning electron microscopy (FE-SEM). The crystallinity of ZnO thin films was characterized by X-ray diffraction (XRD). Analysis of optoelectronic

(a)

(b)

FIGURE 2: SEM images of the as-deposited ZnO thin films on the ONPS layer. (a) The cross-sectional view and (b) the top view.

characteristics of photodiodes was carried out by a photore-sponse measurement system with a TRIAX320 spectrometer. The current-voltage characteristics of devices were measured by an HP-4155A semiconductor parameter analyzer.

3. Results and Discussion

Figure 2 showed the SEM images of samples with the as-deposited ZnO thin films on ONPS buffer layers. From Figure 2(a), the cross-sectional view of the sample, we can observe that a ZnO thin film with thickness of about 100 nm was deposited on a $3.5\text{ }\mu\text{m}$ ONPS layer that was prepared on a Si substrate. As shown in Figure 2(b), the top view of the sample, the deposited ZnO film had a smooth surface and contained uniformly distributed grains with average sizes of about 20 nm~30 nm.

X-ray diffraction (XRD) patterns of the deposited ZnO film on ONPS at different annealing temperatures were shown in Figure 3. The obtained ZnO film had a polycrystalline structure with two obvious diffraction peaks at 34.395° and 62.78° , which are corresponding to ZnO (002) and ZnO (103), respectively. The intensity of diffraction peak increased with the annealing temperature, indicating that the crystallinity of the ZnO films was improved at higher annealing temperatures.

FIGURE 3: X-ray diffraction patterns of ZnO films deposited on ONPS layers of Si substrates for different annealing temperatures.

FIGURE 4: Selected X-ray diffraction patterns of ZnO films deposited on different substrates.

Figure 4 showed the selected X-ray diffraction patterns of ZnO films deposited on different substrates for $2\theta = 33^\circ \sim 35.5^\circ$. We can observe that the value of full width at half maximum (FWHM) of the main peak for the ZnO film deposited on ONPS was approximately equal to that of the ZnO on NPS, while it was lower than that of ZnO on Si. This result confirmed that the film quality of ZnO deposited on NPS or ONPS was better than that on a bare Si substrate and indicated both NPS and ONPS buffer layers can help to improve the film crystallinity of ZnO hetero growth on a Si substrate.

Figure 5 illustrated the photoresponse spectra of ZnO photodiodes fabricated on Si substrates with NPS or ONPS buffer layers. It was found that ZnO-on-NPS devices had high responsivity to the 300~400 nm UV light, but they also strongly respond to the 600~1000 nm irradiation which

FIGURE 5: Photoresponse spectra of ZnO photodiodes prepared on Si substrates with NPS and ONPS buffer layers, respectively. For comparison purpose, the photoresponse spectra of a bare NPS layer on a Si substrate were also included in the figure.

corresponded to the visible-to-IR light. It is disadvantageous to exhibit visible and IR response for a UV photodetector for some special purposes. To clarify the origin of the non-UV photoresponse, the photoresponse spectra of a bare NPS layer prepared on a Si substrate were also measured and also shown in Figure 5. It was observed that the photoresponse of NPS-on-Si mostly appeared within visible-to-IR regions. In addition, the optical bandgap of the prepared NPS and ZnO films that was measured from Tauc's plots was 1.6 eV and 3.2 eV, respectively. Thus, it can be inferred that the visible-to-IR response of a ZnO-on-NPS device mainly came from the light absorption of NPS layers. In order to restrict the non-UV absorption, NPS layers were converted into ONPS with a RTO process before the ZnO deposition. It was found the ZnO-on-ONPS device achieved high 300~400 nm UV photoresponsivity as shown in Figure 5. Most importantly, the visible-to-IR photoresponse above 500 nm almost disappeared in these devices. Because the optical bandgap of ONPS measured from Tauc's plots was about 3.5 eV that corresponded to an absorption wavelength of 350 nm, an ONPS layer was only sensitive to UV light. That is, the ONPS buffer layer not only contributed UV response to devices but also largely suppressed the visible-to-IR response originating from the light absorption of Si substrates. Therefore, UV-to-visible/IR rejection ratio of the developed ZnO photodiode fabricated on a Si substrate can be greatly enhanced by introduction of an ONPS buffer layer.

Current-voltage characteristics of the ZnO-on-ONPS photodiode with and without UV illumination were shown in Figure 6. The photocurrent was measured under irradiating light with wavelength of 375 nm and power of 0.08 mW/cm^2 . At a 5-V bias, the measured photocurrent was 4.74 mA/cm^2 and the dark current was $4.56 \times 10^{-2} \text{ mA/cm}^2$. The photo-to-dark current ratio (PDCR) was calculated up to about 104, indicating that the developed device was highly sensitive to UV light.

FIGURE 6: Current-voltage characteristics of the ZnO photodiode fabricated on a Si substrate with an ONPS buffer layer.

4. Conclusions

ZnO thin films with smooth surfaces and uniformly distributed grains had been successfully deposited on Si substrates with NPS and ONPS buffer layers. XRD measurement showed that the crystallinity of the deposited ZnO thin films on both buffer layers was better than that deposited directly on Si substrates. ZnO-on-NPS devices exhibited high UV and visible-to-IR photoresponsivity. The undesirable visible-to-IR response above 500 nm was almost eliminated in ZnO-on-ONPS devices. The developed ZnO-on-ONPS photodiodes achieved high photocurrent and high PDCR, demonstrating that ZnO on ONPS had high potential in the development of low-cost UV photodetectors.

Conflict of Interests

The author declares that he has no competing interests.

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