Effects of annealing temperature on the characteristics of Ga-doped ZnO film metal-semiconductor-metal ultraviolet photodetectors

L. C. Yang,[1,2] R. X. Wang,[1,a)] S. J. Xu,[1,3] Z. Xing,[1] Y. M. Fan,[1] X. S. Shi,[2,4] K. Fu,[1] and B. S. Zhang[1]
[1]*Suzhou Institute of Nano-tech and Nano-bionics, Chinese Academy of Sciences, Suzhou 215123, China*
[2]*The 41st Research Institute of CETC, Qingdao 266555, China*
[3]*Department of Physics and HKU-CAS Joint Laboratory on New Materials, The University of Hong Kong, Pokfulam Road, Hong Kong*
[4]*Science and Technology on Electronic Test & Measurement Laboratory, Qingdao 266555, China*

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Metal-semiconductor-metal ultraviolet photodetectors were fabricated by using the sputtered Ga-doped ZnO (GZO) thin films on sapphire substrate as an active layer. Current-voltage (I-V) and opto-electrical characteristics of the devices were investigated. It is found that the peak optical responsivity of the devices can be significantly improved by selecting appropriate thermal annealing temperature, i.e., from 12.0 A/W (annealed at 500 °C) and 54.0 A/W (700 °C). Furthermore, dark current of the devices drops by two orders of magnitude after annealing process. The significant improvement in performance of the device is ascribed to the removal of massive defect centers of the GZO thin films and increase of Schottky barrier height between the GZO and metal electrodes after thermal annealing at appropriate temperatures. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4791760]

I. INTRODUCTION

The development of ultraviolet (UV) photodetectors (PDs) has been driven by its increasingly vast applications in defense, space monitoring, flames safeguard, fire control, and other numerous areas. For these applications, UV PDs need efficient UV opto-electrical responses and their fabrication requires active materials showing UV photoresponse, for example, some wide band gap semiconductors[1–8] such as gallium nitride,[1] zinc oxide (ZnO),[2] and silicon carbide.[3] Compared with GaN-based materials, ZnO and related materials are an attractive alternative material due to its advantages such as low cost, easy preparation, and low growth temperature.[4–8]

Photodetectors with metal-semiconductor-metal (MSM) structures are an example of widely demonstrated photoconductive devices. Commonly, Schottky-contact-based photovoltaic or ohmic-contact-based photoconductive devices are adopted for the MSM structured PDs and in comparative, it is easier for a photoconductive detector to achieve a higher gain than a photovoltaic detector.[4]

Compared with pure ZnO, doped ZnO can consist of some very different properties. For one, doping ZnO can alter its electrical conductive properties. Group III elements, i.e., Ga, Al, In, and some group VII elements, i.e., I and Cl can be used as n-type dopants in ZnO to influence the electrical properties of the materials.[9] Among them, Ga dopant has been proposed to be advantageous because smaller lattice deformation is expected even in the case of high Ga concentration.[10,11] It is also worthy to note that it is possible for the effective band gap Ga-doped ZnO (denoted by GZO hereafter) to be expanded over 4.4 eV.[12] Several methods can be used to deposit GZO thin films, including sputtering, pulsed laser ablation, dip coating, and so on. Transmittance of GZO thin films can be over 80% in visible light range and electrical resistivity as low as 10^{-3} Ω cm.[13–15] These advantages have stimulated researchers to grow GZO thin films and develop GZO based photodetectors.[16–18]

In this article, we report a type of efficient MSM UV detectors fabricated by using GZO thin films on sapphire substrates. After the devices are annealed in oxygen ambient at 700 °C, the UV responsivity of the devices can be significantly increased from 0.004 to 54.0 A/W under a 10.0 V bias voltage for 360 nm wavelength. In order to explore the enhancement mechanism, the structural and opto-electrical properties of the GZO thin- film PDs are investigated in detail. The results reveal that improvement in crystal quality of the thin films and in the metal-GZO Schottky contact after thermal treatment should be responsible for the observed enhancement of the device's responsivity in UV spectral region.

II. EXPERIMENTAL

Before the GZO thin film sputtering, *c*-plane sapphire substrates were cleaned in an ultrasonic cleaner for 5 min with acetone and ethanol and successively dried with nitrogen gas. Thereafter, the GZO thin film was deposited on a clean sapphire substrate with radio frequency magnetron sputtering technique using a ZnO mixture with Ga_2O_3 as the target. MSM GZO PDs with two interleaved fork-shapes were prepared with Ni/Au thin films deposited by e-beam evaporation. Standard lift-off procedures were then used to make MSM structures, as shown schematically in Fig. 1(a). As seen from the top-view SEM image of the device electrode pattern in Fig. 1(b), the device active area is $500 \times 500\ \mu m^2$ with 10 μm/10 μm finger width/spacing. After

a)Author to whom correspondence should be addressed. Electronic mail: rxwang2008@sinano.ac.cn.

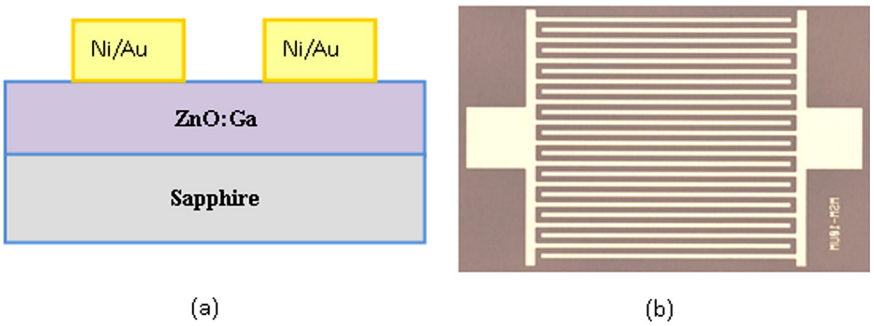

FIG. 1. (a) Cross-sectional schematic structure diagram of the GZO based MSM type PDs; (b) top view SEM image of the PDs.

the preparation procedures stated above, the samples were annealed in oxygen gas for 30 min at 500 °C and 700 °C, respectively.

Room-temperature current-voltage (I-V) characteristics of the prepared PDs were measured using Keithley 4200 parameter analyzer. Spectral responsivity of the PDs was measured using a Xe arc lamp as the light source along with a 250-nm-blaze grating calibrated monochromator, an optical chopper, and a lock-in amplifier in a synchronous detection scheme. Output power of the monochromatic light was calibrated with a commercial Si PD. Spectral responsivity measurements were carried out at different bias voltages for the PDs illuminated from front. Crystal structures of the films on sapphire substrate were examined with a D8 advance x-ray diffractometer (XRD) at room temperature.

III. RESULTS AND DISCUSSIONS

Figure 2 shows measured room-temperature I-V characteristics of the fabricated devices as-deposited (solid line), annealed at 500 °C (dashed line), and 700 °C (dashed-dotted line) under dark conditions. It is found that the dark current of the devices shows a surprisingly large dependency on the annealing temperature. Compared with the as-prepared device, the dark current of the annealed PDs reduces by almost two orders under the same applied voltage. In order to understand the physical mechanism of this remarkable reduction of the PDs' dark current after thermal annealing, we conducted Hall transport measurements on the as-deposited and annealed GZO thin films at room temperature. The Hall data of the thin films are listed in Table I. From Table I, it can be seen that both the electron concentration and mobility of the thin films show a significant dependence on the annealing temperature. To reason such a phenomenon, according to Ohm law, it is well known that current density of one conducting material is equal to the product of applied electric field and electrical conductivity of a material. From a Drude picture of electron transport in solid state materials, electrical conductivity is proportional to a product of electron concentration and mobility.[19] When compared with the as-deposited sample, there indeed was a decrease in the product of electron concentration and mobility of the annealed samples. Furthermore, based on thermal emission mechanism model,[19] dark current of a metal-semiconductor Schottky contact shows a distinct dependence on the contact barrier height, i.e., $I_d \propto e^{-q\phi/kT}$, where ϕ is the barrier height, k is the Boltzmann constant, and T is the temperature. In the present work, the derived barrier heights are 0.45, 0.57, and 0.58 eV for the devices as-deposited, annealed in oxygen ambient at 500 °C and 700 °C, respectively. The increase in the Schottky barrier height after the thermal annealing leads to strong suppression of the dark leakage current of the devices.

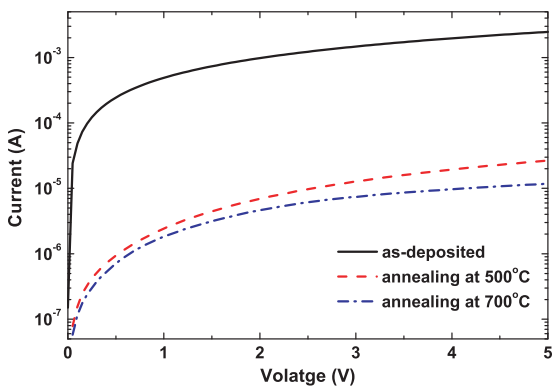

FIG. 2. The dark current-voltage characteristics of the PDs prepared with the as-deposited (solid line) and annealed GZO thin films at 500 (dashed line) and 700 °C (dashed-dotted line).

More interestingly, the optical responsivity of the devices is observed to increase greatly, for example, from 0.004 A/W of the as-prepared device to 54.0 A/W of the annealed device in oxygen ambient at 700 °C when a 10.0 V voltage is applied under the illumination of 360 nm light, as listed in Table I. It is observed that the photoresponse of as-deposited PD measured at UV and visible range remains almost unchanged while much improvement is observed in the photoresponse of annealed PDs. In fact, optical response of the PDs can be improved greatly over a wide wavelength range. Figure 3 shows the measured spectral responses of the PDs as-deposited and annealed at different temperatures. From the figure, it can be seen that the optical responsivity in a wavelength range of 260–450 nm is radically enhanced by thermal annealing. Moreover, the optical responsivity of the

TABLE I. The properties of the GZO films: as-deposited and annealed at different temperatures.

	As-deposited	Annealed at 500 °C	Annealed at 700 °C
XRD (FWHM/deg)	2.37	2.01	1.55
Mobility ($cm^2/V\,s$)	1.70	3.06	4.76
Electron concentration (cm^{-3})	2.29×10^{19}	6.64×10^{17}	4.48×10^{17}
Optical responsivity (at 360 nm) at 10.0 V bias (A/W)	0.004	12.0	54.0

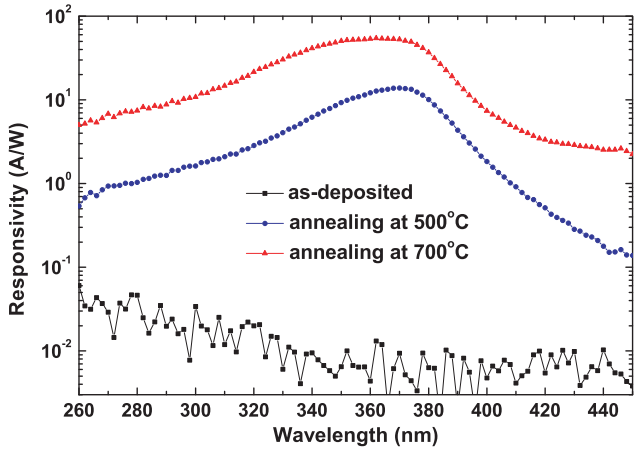

FIG. 3. Optical responsivity of the PDs under a 10 V bias (prepared with the GZO thin films as-deposited and annealed at different temperatures).

annealed PDs further improves with increasing annealing temperature, i.e., the responsivity value at 360 nm can be increased by 5 times when the annealing temperature raises from 500 °C to 700 °C. These results firmly show that the spectral responsivity of the PDs fabricated using sputtered GZO thin film can be significantly improved by using thermal annealing process. We know from definition that optical responsivity is proportional to photocurrent intensity and reversely proportional to power of incident light. Therefore, the photocurrent of the devices after thermal treatment should increase significantly when the bias voltage is kept unchanged.

The dramatic drop in dark current and simultaneous increase in photocurrent after the thermal annealing of the PDs means major improvement to the GZO thin-film PDs' performance. The improvement in crystal quality of the GZO thin films and increase in Schottky contact height after the thermal treatment should be responsible for such improvement.[20] In order to test the idea, XRD measurements on the as-deposited and annealed samples were performed. Figure 4 shows the XRD scanning (θ–2θ) and rocking curves

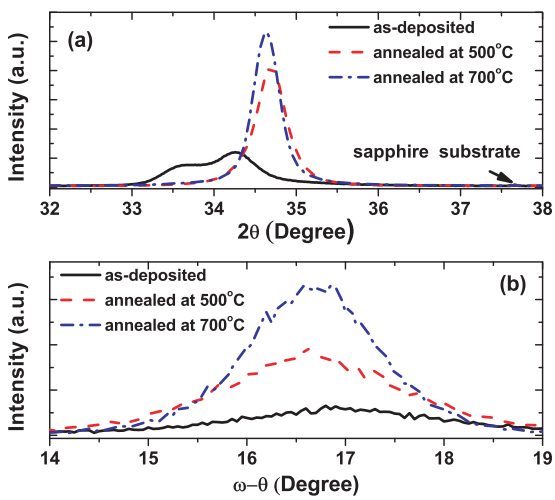

FIG. 4. The θ–2θ (top) and $\omega-\theta$ (bottom) XRD curves of the GZO thin films as-deposited and annealed at different temperatures on sapphire substrates.

(ω–θ) of the as-deposited and annealed GZO films. For the as-deposited film, a dominant peak at 34.2° in scanning (θ–2θ) curve is the diffraction peaks from the (002) crystalline planes of hexagonal wurtzite ZnO, this is consistent with others' report.[20,21] The weaker peaks at 33.6° and 37.6° are the diffraction peaks from (111) crystalline planes of gallium oxide and sapphire substrate, respectively. For the annealed films, the peak of zinc oxide becomes much stronger and narrower while the peak of gallium oxide becomes virtually unobservable. This indicates that the crystal quality of the sputtered GZO thin film is greatly improved after thermal annealing. Furthermore, the (002) diffraction peak of ZnO shifts to 34.6° after the 700 °C thermal treatment, indicating that the lattice parameter c of the annealed film becomes closer to that of ZnO bulk crystal. The XRD rocking curves (ω–θ) also prove that the crystal quality of the thin film is largely improved from the thermal annealing. Peak intensity increases and at the same time the full width at half maximum (FWHM) of the ZnO (002) diffraction peak reduces from 2.37° to 1.55° when the as-deposited thin film was thermally annealed at 700 °C. These XRD data unambiguously show the improvement of crystal structure is largely due to removal of structural defects in the films and strain relaxation between the GZO thin film and sapphire substrate.[10,20,21] As a result of such improvement in crystal structure after the thermal treatment, the metal-GZO Schottky contact is significantly improved, i.e., the increase in barrier height. The dark leakage current of the devices is thus exponentially reduced, as observed in Fig. 1. Moreover, the thermal removal of massive structural defects in the thin film can prolong the lifetime of photo-excited carriers, which is strongly positive to photocurrent, as argued below, since various defects usually act as the killers of carriers and thus shortening its lifetimes, especially the photo-excited carriers in semiconductors and luminescent materials.

Figures 5(a) and 5(b) show the measured optical responsivity of the PDs annealed at 500 °C and 700 °C under different bias voltages, respectively. It can be observed that the responsivity of the annealed devices increases when increasing applied bias voltage. The optical responsivity of the PDs annealed at 700 °C increases faster than that of the PDs annealed at 500 °C with increased applied voltage, as seen in Fig. 6 in which the measured responsivity (symbols) of the PDs annealed at 500 and 700 °C for 360 nm excitation wavelength is depicted for different bias voltages. These results indicate that 700 °C thermal annealing is more effective than 500 °C for improving the performance of GZO thin-film PDs.

For a photoconductive device, its gain G can be expressed as[19]

$$G = \frac{V(\mu_n + \mu_p)\tau}{L^2}, \tag{1}$$

where V, μ_n, μ_p, τ, and L are applied voltage, mobility of electron and hole, lifetime of carriers, and separation length between electrodes, respectively. Equation (1) clearly shows how the performance of a photoconductive detector can be improved. From Table I, the electron mobility of the GZO

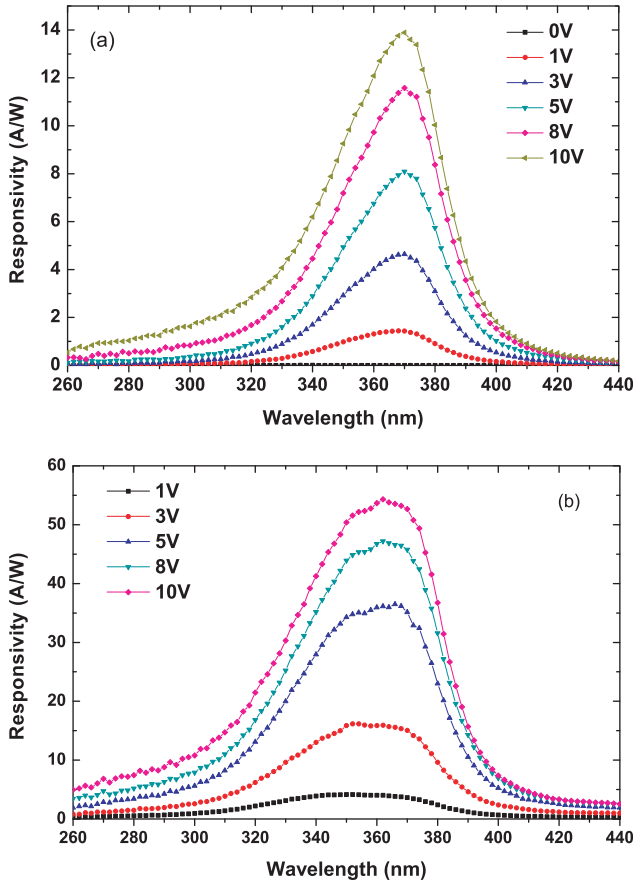

FIG. 5. Optical responsivity of the GZO PDs annealed at (a) 500 °C and (b) 700 °C, under the different bias voltages.

thin film annealed at 700 °C is much larger than that of the as-deposited one. According to Eq. (1), the PDs fabricated by using the GZO thin film annealed at 700 °C could achieve a much higher gain.

Another key factor identified is the carrier's lifetime. As argued earlier, 700 °C annealing could lead to improvement of crystalline structure quality and suppression of defect centers in the GZO thin film when compared to 500 °C annealing. It is well known that defect centers usually act as recombination centers of carriers in semiconductor materials. Suppression and even removal of defect centers would elongate the lifetime of carrier.

From Eq. (1), we know that gain is basically proportional to applied voltage. Indeed, the measured responsivity of the PDs annealed at 500 and 700 °C shows a linear dependence on applied voltage, as indicated by the solid lines (the linear fitting lines) in Fig. 6. For the PD annealed at 700 °C, electron mobility of the GZO thin film is higher than that of the thin film annealed at 500 °C and the lifetime of carriers is longer. Therefore, the optical responsivity of the 700 °C annealed PDs exhibits a larger dependence on the bias voltage according to Eq. (1).

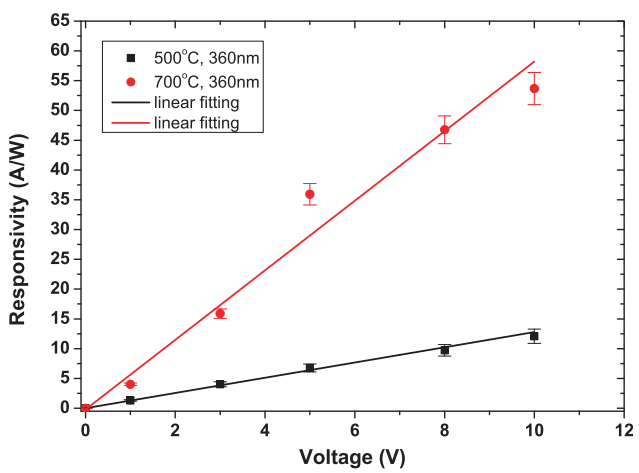

FIG. 6. Responsivity dependence of the GZO PDs annealed at 500 °C and 700 °C on the bias voltage for 360 nm excitation wavelength. The solid symbols represent the measured data while the solid lines are the linear fitting curves.

IV. CONCLUSIONS

The GZO thin films sputtered on sapphire substrates were used as active layer for the fabrication of MSM structured UV photodetectors. Electrical and structural properties of the GZO thin films were investigated by Hall measurement and XRD, respectively. It is found that the overall performance of the devices can be greatly improved by using an appropriate temperature thermal annealing.

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