The Effect of Annealing Ambience on the Material and Photodetector Characteristics of Sputtered ZnGa$_2$O$_4$ Films

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Abstract: Spinel ZnGa$_2$O$_4$ films were grown on c-plane sapphire substrates at the substrate temperature of 400 °C by radio-frequency magnetron sputtering. Post thermal annealing was employed at the annealing temperature of 700 °C in order to enhance their crystal quality. The effect of thermal annealing on the microstructural and optoelectronic properties of ZnGa$_2$O$_4$ films was systematically investigated in various ambiances, such as air, nitrogen, and oxygen. The X-ray diffraction patterns of annealed ZnGa$_2$O$_4$ films showed the crystalline structure to have (111) crystallographic planes. Transmission electron micrographs verified that ZnGa$_2$O$_4$ film annealed under air ambience possesses a quasi-single-crystalline structure. This ZnGa$_2$O$_4$ film annealed under air ambience exhibited a smooth surface, an excellent average transmittance above 82% in the visible region, and a wide bandgap of 5.05 eV. The oxygen vacancies under different annealing ambiences were revealed a substantial impact on the material and photodetector characteristics by X-ray photoelectron spectrum investigations. ZnGa$_2$O$_4$ film exhibits optimal performance as a metal-semiconductor-metal photodetector when annealed under air ambience. Under these conditions, ZnGa$_2$O$_4$ film exhibits a higher photo/dark current ratio of ~10$^4$ order, as well as a high responsivity of 2.53 A/W at the bias of 5 V under an incident optical light of 240 nm. These results demonstrate that quasi-single-crystalline ZnGa$_2$O$_4$ films have significant potential in deep-ultraviolet applications.

Keywords: ZnGa$_2$O$_4$; annealing ambience; wide bandgap; metal-semiconductor-metal photodetector; responsivity

1. Introduction

Deep-ultraviolet photodetectors (DUV PDs) based on ZnGa$_2$O$_4$ films are of substantial interest due to their prospective applications in flame monitoring, missile threat detection, ozone hole monitoring, engine control, optical communication, aerospace, and lithography alignment [1–4]. The high electrical conductivity and high electrochemical activities of ZnGa$_2$O$_4$ make it suitable for use as an anode material in rechargeable batteries [5]. ZnGa$_2$O$_4$ is a well-known phosphor material due to its intrinsic blue emission characteristics, which may be shifted to other emission wavelengths by doping metal ions or surface defects. It also exhibits a variety of functional features that can be applied to optoelectronic devices [6,7]. ZnGa$_2$O$_4$ possesses a wide bandgap in the region of 4.4–5.2 eV [8,9]. Its inherent chemical and thermal characteristics in a harsh environment along with high breakdown voltage make ZnGa$_2$O$_4$ a potential candidate for high-voltage devices, such as transistors and MOSFETs [10]. Wide bandgap semiconductors improve the efficiency of power-conversion stages, and they may be utilized instead of silicon in the production of voltage converters, power MOSFETs, and high-efficiency Schottky diodes. These can
then be employed in electric and hybrid cars [11]. Recently, Chi et al. and Chikoidze et al. demonstrated the p-type ZnGa$_2$O$_4$ semiconductor (5 eV), which could pave the way for bipolar oxide energy electronics by reducing switching and conversion losses. This is due to ZnGa$_2$O$_4$’s combination of the required qualities for sustaining large electrical fields in p-n junctions in the off-state, together with low losses in the on-state [12,13]. ZnGa$_2$O$_4$ possesses the cubic symmetric spinel structure with the space group of Fd3m, where Zn$^{2+}$ cations occupy tetrahedral sites and Ga$^{3+}$ cations occupy octahedral sites with oxygen atoms in close-packed cubic structures [11,14].

There are other wide bandgap semiconductors such as $\beta$-Ga$_2$O$_3$ and (Al$_x$Ga$_{1-x}$)$_2$O$_3$, but these require high growth temperatures as well as high post-thermal annealing temperatures in order to create high-quality epitaxial films to employ in DUV spectral selection. Besides this, its anisotropic structural, optical, thermal, and mechanical characteristics including easy cleaving are the other drawbacks associated with $\beta$-Ga$_2$O$_3$. These drawbacks can be overcome using spinel ZnGa$_2$O$_4$, which offers a higher electrical conductivity, an isotropic cubic structure, distinguishable Zn and Ga cation sites, and a stable phase [15]. ZnGa$_2$O$_4$ is found to be suitable for use as the active layer in the fabrication of DUV PDs due to its insensitivity to light above the wavelength of 280 nm. Optoelectronic devices fabricated with one-dimensional nanostructures, such as nanotubes, nanowires, and nanocrystals, can achieve a high photoelectric conversion efficiency. However, in practice their stability and repeatability are still major concerns [16–18]. Hence, the development of ZnGa$_2$O$_4$ film-based PDs is essential. ZnGa$_2$O$_4$ films have been reported earlier by several research groups using radio-frequency (RF) magnetron sputtering [19,20], pulsed laser deposition [21], metal-organic chemical vapor deposition (MOCVD) [22], and mist-CVD [23]. Among these, RF magnetron sputtering is a cost-effective and dependable technology that is extensively utilized by industrial processes to build commercial optoelectronic devices. This is due to its ability to deposit films with a high purity, excellent compactness, repeatability, and homogeneity across a large area in less time than that taken by other technologies.

In this study, RF magnetron sputtering is used for depositing ZnGa$_2$O$_4$ films. The microstructural and optoelectronic characteristics of ZnGa$_2$O$_4$ films have been systematically investigated using an X-ray diffractometer, transmission electron microscope, atomic force microscope, field-emission scanning electron microscope, N&K analyzer, Keithley semiconductor parameter analyzer, and deuterium lamp with an Omni spectrometer. To date, the ambient effects of these thermal annealing processes have not been explored when assessing the material and photodetector characteristics of ZnGa$_2$O$_4$ films on sapphire substrates using RF magnetron sputtering.

2. Materials and Methods

ZnGa$_2$O$_4$ films (200 nm thickness) were deposited on 2-inch c-plane sapphire (0001) substrates using RF magnetron sputtering (model: SP-203, LHUHV, Hsinchu, Taiwan). The 3-inch ceramic target of ZnGa$_2$O$_4$, which had a purity of 99.99% (with a 50/50 ratio of ZnO/Ga$_2$O$_3$), was taken into consideration. The substrate was cleaned with acetone, isopropyl alcohol, and distilled water separately. It was then blow-dried with nitrogen gas before being introduced into the deposition chamber. When the base pressure had reached $1 \times 10^{-6}$ Torr, the deposition of films was performed at the working pressure of $5 \times 10^{-3}$ Torr and the substrate temperature of 400 °C. The rotation of the sample stage was maintained at 10 rpm to achieve a uniform thickness. The flow rate of argon gas was maintained at 10 sccm. Prior to sputtering, the target was pre-sputtered for 10 min by covering the target of the shutter in order to remove impurities on the surface of the ZnGa$_2$O$_4$. After this, the plasma was ignited by directing 100 W of RF power on the ceramic ZnGa$_2$O$_4$ target. As-deposited films were thermally annealed at a temperature of 700 °C using rapid thermal annealing (RTA, RTP-T41, Premtek International Inc., Hsinchu, Taiwan) for 1 min under air, nitrogen, and oxygen ambiances.
The thickness of the films was determined by an α-step profile analyzer. The crystallinity of the films was measured using a X-ray diffractometer (HR-XRD, X’Pert Pro MRD, PANanalytical, Almelo, Netherland). An N&K analyzer (model: 1280, n&k Technologies, San Jose, CA, USA) was used in this investigation to measure the transmittance of the ZnGa$_2$O$_4$ films. The optical bandgap of the films was extracted through Tauc plot. The surface morphology was determined using a field emission scanning electron microscope (FESEM, JSM-6700F, JEOL, Tokyo, Japan). The root-mean-square (RMS) surface roughness of the ZnGa$_2$O$_4$ films was measured using an atomic force microscope (AFM, Dimension 5000, Bruker, Santa Clara, CA, USA). The nanostructure and crystal orientations of the ZnGa$_2$O$_4$ films were studied using a transmission electron microscope (JEM-2100F, JEOL, Tokyo, Japan). The chemical states of the films were characterized by X-ray photoelectron spectroscopy (XPS, PHI 5000 Versa Probe, ULVAC-PHI, Kanagawa, Japan). The X-ray source for XPS was the monochromatized AlKα source (1486 eV). The X-ray beam size and takeoff angle were 100 µm and 45°, respectively. The pass energy was 58.7 eV. High-resolution scans were obtained by averaging 50 scans for O 1s peak in this investigation. Surface charging was minimized by an electron flood gun operated at 3 eV.

The metal-semiconductor-metal photodetector was fabricated with the interdigitated metal Ti/Au (with a thickness of 40/60 nm) Schottky contacts with the help of an electron-beam evaporator. These contacts were specified by photolithography and lift-off techniques. The active areas of the PDs were 1.05 × 1.05 mm$^2$, whereas the length, width, and spacing for the interdigital electrodes were specified as 950, 50, and 50 µm, respectively. The current–voltage characteristics were measured via a Keysight/Agilent semiconductor parameter analyzer (4155B, Hewlett-Packard Company, Englewood, CO, USA). A 30 W deuterium lamp was associated with the spectrometer (Omni-λ3029i, Zolix, Beijing, China) as the light source in the wavelength region of 200–360 nm, which helped us in the measurement of the spectral response of ZnGa$_2$O$_4$ PDs at the bias of 5 V.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of as-deposited and annealed ZnGa$_2$O$_4$ films under different annealing ambiences. As-deposited ZnGa$_2$O$_4$ film exhibited weak Bragg reflections for the (111), (222), and (511) planes, which corresponds to the spinel-cubic ZnGa$_2$O$_4$ (JCPDS card no-381240). The crystallinity of the as-deposited ZnGa$_2$O$_4$ film improved after thermal annealing under different ambiences. The thermal annealing of ZnGa$_2$O$_4$ films under air and nitrogen ambience dramatically increased the intensity of the (111), (222), and (511) planes, indicating that these films had a high crystallinity. In contrast, ZnGa$_2$O$_4$ film annealed under oxygen ambience had a low crystallinity, implying that this as-deposited film became oxidized after thermal annealing under an oxygen atmosphere. This shows that annealing in oxygen ambience can fulfill the oxygen vacancies in the ZnGa$_2$O$_4$ film, which leads to its oxidation and thus slight degradation in its crystallinity.

Figure 2a–h shows the AFM and SEM micrographs of as-deposited and annealed ZnGa$_2$O$_4$ films under different annealing ambiences. As-deposited ZnGa$_2$O$_4$ film exhibited a columnar structure and irregular arrangement of grains with a rough surface, which was found to be dense and smooth after annealing under air and nitrogen ambiences with the presence of some nano-voids. It is well-known that high-temperature annealing reduces the surface energy between grains, which increases grain growth and reduces surface roughness due to the coalescence of small grains [25,26]. ZnGa$_2$O$_4$ film annealed under oxygen ambience was...
found to be oxidized due to the absorption of oxygen in the film, which possesses a dense and highly rough surface with fewer nano-voids than other films [24]. These SEM results were found to be in accordance with the AFM and XRD results.

Figure 1. X-ray diffraction patterns of ZnGa$_2$O$_4$ (ZGO) films under different annealing ambiences.

Figure 3 depicts the cross-sectional and high-resolution transmission electron micrographs (HRTEM) of as-deposited and annealed ZnGa$_2$O$_4$ film under air ambience. The cross-sectional TEM micrograph of as-deposited ZnGa$_2$O$_4$ film is shown in Figure 3a, while region I and region II of this film are explored in Figure 3b,c, respectively. This as-deposited ZnGa$_2$O$_4$ film demonstrated columnar grains near the substrate region and possessed the amorphous, ZnO (100), Ga$_2$O$_3$ (201), and ZnGa$_2$O$_4$ (111) phases. These phases are evident in this film, as it was deposited at a substrate temperature of 400 °C. The d-spacing of ~2.83, 3.70, and 4.83 Å (compatible with 4.80 Å) was measured, which corresponded to the ZnO (111), Ga$_2$O$_3$ (201), and ZnGa$_2$O$_4$ (111) phases, respectively. The rapid thermal annealing was performed at the temperature of 700 °C for 1 min under air ambience to improve the crystallinity of this film. The oxygen present in the air ambience during thermal annealing played a significant role in eliminating the intrinsic defects, such as amorphous regions and oxygen vacancies in the films. A cross-sectional TEM micrograph of the annealed ZnGa$_2$O$_4$ film under air ambience is shown in Figure 3d, and its region I and region II are explored in Figure 3e,f, respectively. These regions (I and II) of the annealed ZnGa$_2$O$_4$ film demonstrated that rapid thermal annealing under air ambience suppressed the amorphous and Ga$_2$O$_3$ phases by the local bond rearrangement at the interface between the amorphous phase and the crystalline phase, and achieved a quasi-single-crystalline ZnGa$_2$O$_4$ structure, as shown in Figure 3e,f.
Figure 2. AFM micrographs of (a) as-deposited, (c) air annealed, (e) N₂ annealed, and (g) O₂ annealed ZnGa₂O₄ films; SEM micrographs of (b) as-deposited, (d) air annealed, (f) N₂ annealed, and (h) O₂ annealed ZnGa₂O₄ films.

Figure 4a shows the transmittance spectrum of the as-deposited and annealed ZnGa₂O₄ films under different annealing ambiances. The average transmittance of the as-deposited and annealed ZnGa₂O₄ films was over 82% in the visible range, with a sharp cut-off in the DUV region. The absorption band-edge of the as-deposited film shifted to shorter wavelengths upon thermal annealing, which demonstrated the improvement in the optical characteristics of this film. Figure 4b shows the Tauc plot, which demonstrates the bandgap values for the as-deposited and annealed ZnGa₂O₄ films under different ambiances. The transmittances values of these films were taken into consideration to calculate the absorption coefficient $\alpha$. The optical bandgap of ZnGa₂O₄ films was obtained using the following relation:

$$(ahv) = A (hν - E_g)^{1/2}$$

(1)

where $A$, $\alpha$, $hν$, and $E_g$ represent the constant, absorption coefficient, energy of the incident photon, and the bandgap energy, respectively. The narrow bandgap of 4.53 eV in the as-deposited ZnGa₂O₄ film can be attributed to the existence of defect states (amorphous structure, phase separations between Ga₂O₃ and ZnO), as shown by TEM (see Figure 3b,c). This led the excited electron to migrate to the conduction band with a low photon energy, narrowing the bandgap. Thermal annealing in various ambiances mitigates the defects.
(including amorphous nature and oxygen vacancies) that are common in as-deposited ZnGa$_2$O$_4$ film. As the thermal annealing was employed, the bandgap increased as 4.98, 5.02, and 5.05 eV under oxygen, nitrogen, and air ambiances, respectively, which allowed this material to lie within the DUV region. It is widely known that materials with a bandgap greater than 4.4 eV absorb UV-C radiation while ignoring visible light, making them ideal for use as high-sensitivity DUV PDs.

**Figure 3.** Cross-sectional and HRTEM micrographs of (a) as-deposited, (b) region I, (c) region II of as-deposited ZnGa$_2$O$_4$ film, (d) annealed, (e) region I, and (f) region II of annealed ZnGa$_2$O$_4$ film under air ambience.

**Figure 4.** (a) Transmittance spectrum and (b) Tauc plot of the as-deposited and annealed ZnGa$_2$O$_4$ films under different annealing ambiances.

Figure 5 shows the O 1s XPS spectra of the as-deposited and annealed ZnGa$_2$O$_4$ films under different ambiances. In order to define the oxygen vacancies associated with the films, the O 1s XPS spectra of the films were fitted with the Gaussian function and deconvoluted into two peaks named O$_I$ and O$_{II}$. The O$_I$ peak centered around the lower binding energies of 530–531 eV represents the oxygen deficiency in the films, whereas the O$_{II}$ peak centered at higher binding energies of 531–532 eV represents the oxygen vacancies in the film [27]. The integrated areas of the O$_{II}$ peak of the ZnGa$_2$O$_4$ films were found to be 43.9, 41.1, 45.3, and 37.6% for as-deposited, air annealed, N$_2$ annealed, and O$_2$ annealed ambiances, respectively. The oxygen present in the air ambience can
fill a certain amount of oxygen vacancy. Hence, the area of O$_{II}$ peak was found to be decreased from 43.9 to 41.1% during air annealing, as shown in Figure 5b. The area of the O$_{II}$ peak was found to be higher (45.3%) in an N$_2$ atmosphere, which can be attributed to the disassociation of oxygen molecules from the films during annealing. This resulted in an increased number of oxygen vacancies, as shown in Figure 5c [25]. By observing the integrated areas of O$_{II}$ peaks from Figure 5a–d, it was found that the O$_2$-annealed ZnGa$_2$O$_4$ film had the lowest integrated area of O$_{II}$ peaks (37.6%). It is well-known that an oxygen-rich ambience reduces the number of oxygen vacancies, which weakens the crystalline structure [28]. This phenomenon is in accordance with our XRD results, as shown in Figure 1, where oxygen ambience deteriorated the crystalline structure. Since oxygen vacancies affect the optoelectronic properties of ZnGa$_2$O$_4$ film, the considerable suppression of oxygen vacancies demonstrates the tunability of the film characteristics depending on the annealing ambiences.

Figure 5. O 1s XPS spectra of (a) as-deposited, (b) air annealed, (c) N$_2$ annealed, and (d) O$_2$ annealed ZnGa$_2$O$_4$ films.

Figure 6 shows the I–V characteristics of the as-deposited and annealed ZnGa$_2$O$_4$ PDs under different annealing ambiences. The as-deposited ZnGa$_2$O$_4$ PD exhibited the photocurrent and dark current of $5.69 \times 10^{-8}$ A and $5.77 \times 10^{-12}$ A, respectively. This photocurrent had decreased from $5.69 \times 10^{-8}$ to $6.12 \times 10^{-9}$ A after annealing under oxygen ambience. This decreased photocurrent can be ascribed to the fulfilment of oxygen vacancies during high temperature annealing under oxygen ambience, which oxidized the ZnGa$_2$O$_4$ films and resulted in the decreased value of photocurrent. Nitrogen ambience
caused the desorption of oxygen atoms from the surface of the films, and created oxygen vacancies, which drastically increased the photocurrent of the as-deposited ZnGa$_2$O$_4$ PD from $5.69 \times 10^{-8}$ to $9.64 \times 10^{-6}$ A. The dark current of as-deposited ZnGa$_2$O$_4$ PD was also found to be increased from $5.77 \times 10^{-12}$ to $3.33 \times 10^{-7}$ A upon annealing this film under nitrogen ambience, which was not desirable for PDs. This high dark current value can be attributed to the high number of inherent defects in the ZnGa$_2$O$_4$ PDs, such as oxygen vacancies and high surface density states, which can result in trapping states and was responsible for a higher internal gain. As a result, these surface states enhanced the dark current as well as the nonradiative recombination for the ZnGa$_2$O$_4$ film (annealed under nitrogen ambience). Similar results have been observed by Tsai et al. in their work [29], where surface related defects were the main cause of the large leakage current in their device, which acted as the adsorption site and captured the free electrons in ZnGa$_2$O$_4$ films. When air ambience was used for annealing, ZnGa$_2$O$_4$ PD exhibited a photocurrent of $2.02 \times 10^{-7}$ A, a dark current of $5.35 \times 10^{-12}$ A, and a $I_{ph}/I_{dark}$ of $3.77 \times 10^4$. Annealing ZnGa$_2$O$_4$ film under air ambience can fill a significant proportion of oxygen vacancies from the oxygen present in the air ambience, which exhibits the enhancement in optoelectronic characteristics of this ZnGa$_2$O$_4$ film and its potential to employ in DUV PDs.

\[ R = (I_{ph} - I_{dark})/P_{inc} \]  

Figure 7 shows the spectral response of the as-deposited and annealed ZnGa$_2$O$_4$ PDs under different annealing ambiences. The spectral response describes the sensitivity of the photodetector to optical radiation of various wavelengths, which is known as the responsivity of the photodetector. This parameter defines the performance of the photodetector and is represented by the following relation:

\[ \text{R} = \frac{I_{ph} - I_{dark}}{P_{inc}} \]  

where $I_{ph}$ is the photocurrent in Ampere (A), $I_{dark}$ is the dark current in Ampere (A), and $P_{inc}$ is the incident optical power in Watt (W). Hence, the responsivity of the photodetector is measured in A/W. As-deposited ZnGa$_2$O$_4$ PD possessed a responsivity of 0.71 A/W, which decreased to 0.12 A/W upon thermal annealing under oxygen ambience. This decreased responsivity could be due to the fulfilment of oxygen vacancies by oxygen gas, which further decreased the mobility of carriers and exhibited the poor responsivity of the ZnGa$_2$O$_4$ PD. Annealing under nitrogen ambience drastically increased the responsivity of ZnGa$_2$O$_4$ PD from 0.71 to 117 A/W. However, N$_2$ annealed ZnGa$_2$O$_4$ PD exhibited a
broad spectral response from the DUV region to the visible region, which was not suitable for the DUV PDs. Annealing under nitrogen ambience reduced the oxygen concentration from the film and generated oxygen vacancy defects and surface density states. These defects led to the creation of deep-trapping centers, which increased the photocurrent as well as the dark current and enhanced the internal gain for ZnGa$_2$O$_4$ PD [29]. Zheng et al. and Han et al. reported that the high responsivity of Mg$_{0.46}$Zn$_{0.54}$O and Mg$_{0.52}$Zn$_{0.48}$O films-based photodetectors is due to the long lifetime of photo-ionized holes, which were found to be trapped at the deep level. This measurement was precisely taken by using deep-level spectral measurement system in their works [30,31]. The trap states of holes include interface states between semiconductor and electrode, surface states, and deep level defects. These trap states were found responsible for this long lifetime phenomenon. It is clear that the photoresponse characteristics of ZnGa$_2$O$_4$ PDs could represent variations due to various oxygen vacancy related defects, which can be suppressed by the adaptation of air ambience. A large amount of oxygen molecules or atoms in the air ambience will diffuse into the samples and fill the significant number of oxygen vacancies, resulting in low surface density states [32]. Annealing under air ambience exhibited both a significant enhancement in the photocurrent and reduction in the dark current by providing adequate energy to compensate the oxygen vacancy related defects. Hence, the responsivity of 2.53 A/W at the given bias of 5 V under the incident optical light of 240 nm was obtained for ZnGa$_2$O$_4$ PD under air ambience. The performance of our fabricated device is compared with that of the previously reported ZnGa$_2$O$_4$ PDs in Table 1.

Figure 7. Spectral response of as-deposited and annealed ZnGa$_2$O$_4$ PDs under different annealing ambiences.

Table 1. Comparison of some key performance of our ZnGa$_2$O$_4$ PD with other previously reported ZnGa$_2$O$_4$ PDs.

| Material       | Growth Method | $I_{\text{dark}}$ (A) | $I_{\text{ph}}$ (A) | $R$ (A/W) | Bias Voltage and $\lambda_{\text{peak}}$ | Reference |
|----------------|---------------|-----------------------|---------------------|-----------|---------------------------------------|-----------|
| ZnGa$_2$O$_4$  | MOCVD         | $-10^{-14}$           | $2.93 \times 10^{-6}$ | 0.203     | 10 V, 260 nm                          | [33]      |
| ZnGa$_2$O$_4$  | MOCVD         | $8.6 \times 10^{-12}$ | $4.04 \times 10^{-8}$ | 0.46      | 10 V, 230 nm                          | [34]      |
| ZnGa$_2$O$_4$  | Sputter       | $2.70 \times 10^{-11}$| -                    | -         | 2 V, 255 nm                           | [35]      |
| ZnGa$_2$O$_4$  | Sputter       | $5.35 \times 10^{-12}$| $2.02 \times 10^{-7}$ | 2.53      | 5 V, 240 nm                           | This work |

Figure 8 shows the rise time and fall time for the as-deposited and annealed ZnGa$_2$O$_4$ PDs under different annealing ambiences. Rise time is the time that the PD takes to change its response from 10% to 90% of the maximum photocurrent with the illumination of light. Fall
time is the time that the PD takes to change its response from 90% to 10% of the maximum photocurrent without the illumination of light. These two characteristics (rise time and fall time) represent the response time of a photodetector. ZnGa$_2$O$_4$ PD annealed under air ambience possesses a higher rise time of 4.55 s but a lesser fall time of 0.19 s than other PDs (as-deposited, annealed ZnGa$_2$O$_4$ PDs under nitrogen and oxygen ambiences), which could be due to the indirect bandgap properties of the spinel-cubic ZnGa$_2$O$_4$ structure [36]. The high rise time for the ZnGa$_2$O$_4$ PD annealed under air ambience could be attributed to the excitation of photogenerated carriers, which reached higher energy states above the conduction band. These excited photogenerated carriers then reverted to the conduction band by releasing energy and resulted in a high rise time. Despite the fact that the response time of ZnGa$_2$O$_4$ PDs annealed in air ambience is higher than that of other ZnGa$_2$O$_4$ PDs annealed under other ambiences, the responsivity associated with this air annealed ZnGa$_2$O$_4$ PD is found to be considerable for use in DUV PDs.

![Time response of as-deposited and annealed ZnGa$_2$O$_4$ PDs under different annealing ambiences](image)

**Figure 8.** Time response of as-deposited and annealed ZnGa$_2$O$_4$ PDs under different annealing ambiences.

4. Conclusions

We have successfully deposited ZnGa$_2$O$_4$ films on sapphire substrates using RF magnetron sputtering, as well as studied the effects of thermal annealing in various ambiences (such as air, nitrogen, and oxygen) on the material and photodetector characteristics of ZnGa$_2$O$_4$ films. Investigations using XRD, AFM, SEM, TEM, N&K analyzer, and DUV measurements revealed that the microstructural and optoelectronic characteristics of ZnGa$_2$O$_4$ films were enhanced under air ambience and affected under nitrogen and oxygen ambiences. These results were verified by comparatively analyzing the chemical states of oxygen on the surface of the ZnGa$_2$O$_4$ films before and after annealing in different ambiences using XPS. The X-ray diffraction patterns of the annealed ZnGa$_2$O$_4$ films exhibited crystalline structures with (111) crystallographic planes. The as-deposited ZnGa$_2$O$_4$ film possessed amorphous regions and phase separations between Ga$_2$O$_3$ and ZnO, which were found to be suppressed after annealing under air ambience. The TEM micrographs revealed that ZnGa$_2$O$_4$ film annealed under air ambience possessed a quasi-single-crystalline structure. The average transmittance of 82% in the visible region and wide bandgap of 5.05 eV were observed for this ZnGa$_2$O$_4$ film. The metal-semiconductor-metal PD fabricated by employing this air annealed ZnGa$_2$O$_4$ film exhibited the high responsivity of 2.53 A/W at the bias of 5 V under the incident light of 240 nm. Besides this, ZnGa$_2$O$_4$ PD had a rise time of 4.55 s, a fall time of 0.19 s, and a photo/dark current ratio of ~10$^4$ order. These results indicate that quasi-single-crystalline ZnGa$_2$O$_4$ films have a high potential to employ in DUV PDs.
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