Fast response ultra-violet photodetectors based on Sol gel derived Ga-doped ZnO

Akshta Rajana, Harish Kumar Yadavb, Vinay Guptaa and Monika Tomarabc,*

aDepartment of Physics and Astrophysics, University of Delhi, Delhi 110007, INDIA
bDepartment of Physics, St. Stephens College, University of Delhi, Delhi 110007, INDIA
cPhysics Department, Miranda house, University of Delhi, Delhi 10007 INDIA

Abstract

Ultraviolet photoconductivity in Gallium doped ZnO (GZO) thin film synthesized by sol-gel technique is investigated. Response characteristics of Pure ZnO thin film and GZO thin film UV photodetector biased at 5 V for UV radiation of $\lambda = 365$ nm and intensity = 24 $\mu$watt/cm$^2$ have been studied. GZO UV photodetector is found to exhibit a high photoconductive gain ($K = 9.32 \times 10^2$) with fast rise and fall time ($T_r = 3$ s and $T_f = 9$ s) in comparison to pure ZnO thin film based photodetector with $K = 4.9 \times 10^1$, $T_r = 6$ s and $T_f = 18$ s. Formation of some neutral atoms at the grain boundaries of GZO thin film due to heavy doping of Gallium in ZnO lattice is the key factor for lowering of dark current ($I_{off} \sim 0.11 \mu$A). Upon UV illumination, the release of trapped electrons from surface defects or adsorbed oxygen results in an enhanced photocurrent ($I_{on} = 0.1$ mA) and hence higher value of $K$ is obtained for GZO thin film based photodetector.

Keywords: ZnO; Doping; Photoluminiscence; UltraViolet detector; Sol-gel processing.

Nomenclature

| Symbol | Description |
|--------|-------------|
| $I_{off}$ | Dark Current |
| $I_{on}$ | Photocurrent |
| $K$ | Photoconductive Gain |
| $T_r$ | Rise time |
| $T_f$ | Fall time |

* Corresponding author. Tel.: +91-987-134-6452.
E-mail address: monikatimar@gmail.com

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1. Introduction

Fabrication of fast and highly sensitive ultraviolet photodetectors is currently in demand in various commercial, military and scientific areas, which has made ultraviolet optoelectronics sensibly an interesting field. In recent years, apart from GaN which is well recognized material for detection of UV rays at commercial level, ZnO thin films and nanostructures have been proved to be beneficial material for photonic device applications due to large exciton binding energy (~60 meV), short carrier lifetime, ease of fabrication of thin films by various deposition techniques, radiation hardness, low cost synthesis etc. [1,2,3,4]. Photoconducting property in ZnO lattice can be significantly improved by replacing Zn atoms with foreign metal atoms such as Al, N, Te, Li and Cu [5,6]. Gallium doped Zinc oxide (GZO) exhibiting similar crystal structure and optical properties as that of GaN and pure ZnO is an optimistic material for such applications. Doping of higher concentration of gallium in ZnO lattice has been reported to decrease its carrier concentration resulting in an increase in the resistivity of ZnO thin film. Moreover, substitution of gallium in sol gel derived ZnO without much lattice distortion is comparatively easier than any other group III elements (Al, In) as the ionic radius of Ga³⁺ (0.62 Å) is smaller than that of Zn²⁺ (0.74 Å) and the covalent band length of Ga–O (1.92 Å) is slightly shorter than that of Zn–O (1.97 Å) [7]. In the present work, feasibility of realizing a fast and highly sensitive UV photodetector has been shown by exploring the photoconducting properties of Ga doped ZnO (GZO) thin film using sol gel technique with 5.5 at. wt % of gallium. Changes in response parameters like dark current, photocurrent, photoconductive gain, rise time and fall time have been studied.

2. Experimental Details

Prior to the fabrication of UV photodetector, platinum inter-digital electrodes (IDEs) were patterned on corning glass substrates using the conventional photolithographic technique. In order to prepare the Pt interdigital electrodes, Pt thin film of 90 nm thickness was deposited by RF sputtering. Finger width and gap width of the patterned electrodes were kept fixed at 500 μm each. In order to prepare the UV photodetector, ZnO and GZO thin films were deposited on the top of patterned electrodes separately as the sensing layer protecting the contact pads and the measurements were carried out through the Pt contact pads of the patterned IDEs. The size of active device area is 1 cm². The schematic of the prepared photodetector is shown in Figure 1.

For the ZnO and GZO thin film deposition, 0.227 M ZnO and GZO sols have been prepared. As a starting material, Zinc acetate dihydrate [Zn(CH₃COO)₂.2H₂O] purchased from Sigma-Aldrich (99.99% pure) was used. Methanol and Monoethanolamine (MEA) were used as a solvent and stabilizer respectively. Zinc acetate dihydrate [Zn(CH₃COO)₂.2H₂O] was first dissolved in a mixture of Methanol and gallium nitrate hydrate (GaNO₃)_x. xH₂O (Fisher scientific, 99.99% pure) and then MEA was added. The prepared solution was spin coated over the IDE/Glass substrates. After each coating, the films were dried at 300ºC for 3-5 min to evaporate the solvent and remove organic residuals. The total thickness of the films was maintained to be 113 nm. The films were annealed at 575ºC for 1 hr in tube furnace to yield the desired crystallinity.

Physical and optical properties of the films were analyzed by X-ray diffraction (XRD), UV-visible spectrophotometer, Photoluminescence spectroscopy and Raman Spectroscopy. The photoluminescence (PL) spectra were obtained at room temperature using a Horiba Jobin Yvon (LabRAM) spectrophotometer with He-Cd laser (λ = 325 nm) to study the defect profile of the pure ZnO and GZO thin films. The Raman spectra was obtained at room temperature using Argon ion laser at
the wavelength of 488 nm to study the defect profile of the deposited thin films. Steady state photoresponse of the fabricated photodetectors was measured at 5 V bias voltage by illuminating the samples using an UV lamp ($\lambda = 365$ nm, intensity = 24 $\mu$watt/cm$^2$) as a radiation source. The photoresponse transients were recorded from semiconductor characterization system (Keithley 4200 SCS). The photoconductive gain of a UV photodetector is defined as $K = I_{on}/I_{off}$ where $I_{on}$ is the photocurrent measured by illuminating the photodetector with UV radiations and $I_{off}$ is the dark current.

3. Results and discussion

3.1. X-ray Diffraction Studies

Figure 2 shows the XRD patterns of ZnO and GZO thin films. It may be seen that both the films exhibit hexagonal wurtzite structure of ZnO. XRD pattern of ZnO thin film shows the dominant reflection corresponding to (002) plane. Although it can be observed from Fig.2 that the relative intensity of dominant (002) peak decreases with respect to intensities of (101) and (100) peaks after incorporating Ga$^{3+}$ ions in ZnO lattice resulting in some deterioration in the crystallinity [8]. The estimated value of the crystallite size for 113 nm thin ZnO film was found to be around 22 nm. On incorporating Ga as dopant in ZnO thin film, crystallite size decreases to 20 nm. Ga-doped ZnO thin film exhibits smaller crystallite size in comparison to that of pure ZnO films due to the fact that Ga has smaller radius compared to Zn [9].

![XRD spectra of ZnO and GZO thin films.](image)

3.3. UV-Visible Spectroscopy

Figure 3 shows the UV-Visible spectra of the ZnO and GZO thin films. Both the films (ZnO and GZO) were found to be highly transparent having about 90% transparency in the visible region. Slight increase in the transparency can be seen for GZO thin film compared to pure ZnO thin film. Optical band gap ($E_g$) of films was evaluated by extrapolating the linear portion of Tauc plot between $(\alpha h \nu)^2$ versus $h \nu$ to $\alpha = 0$, where $\alpha$ is the absorption coefficient and $h \nu$ is the photon energy. Estimated value of the band gap was found to be 3.276 eV for the pure ZnO thin film and is in good agreement with the values reported by other workers for ZnO thin films grown by various techniques [10]. The band gap was found to increase from 3.276 eV to 3.29 eV with the incorporation of Ga in the ZnO thin film (inset of Figure 3). Increase in band gap after doping of Ga in ZnO lattice is attributed to degraded crystallinity and reduced grain size as seen in XRD spectra [11].
3.4. Raman scattering spectroscopy

Figure 4 (A and B) show the room temperature Raman spectra of pure ZnO and GZO thin films. The characteristic optical modes of wurtzite ZnO at 99 and 437 cm\(^{-1}\) corresponding to the \(E_2^{\text{low}}\) and \(E_2^{\text{high}}\) modes respectively were observed fig 4(A). The peak at 303 cm\(^{-1}\) and 524 cm\(^{-1}\) observed in Raman spectra of pure ZnO is due to the scattering from the silicon substrate [12]. It is reported in literature that when Ga is doped in ZnO lattice an additional mode at 505 cm\(^{-1}\) appears in the Raman spectra of GZO thin film (fig.4 (B)), which is attributed to the free charge carriers [13]. In the present work, it is difficult to identify 505 cm\(^{-1}\) band in the Raman spectra of GZO film due to the presence of strong mode of the silicon substrate.

3.5. Photoluminescence Studies

The room temperature photoluminescence (PL) spectra obtained for pure ZnO and GZO thin films are shown in Fig.5. Two emission peaks centred at around 3.3 eV and 2.4 eV were observed in PL spectra of both of the films (Fig.5). The peak at around 3.3 eV is the characteristic emission peak for ZnO corresponding to the near band edge (NBE) emission and is expected to arise from the recombination of free exciton [14]. The other broad emission peak (~ 2.4 eV) in the visible region (Fig.5) corresponds to the deep level emission arising due to the presence of point defects in the GZO thin films. Blue Shift in the energy of NBE peak has been observed for GZO thin film which shows an increase in band gap of ZnO after doping gallium and is in accordance with the UV-visible studies. This might be due to quantum size effect caused by segregation of...
some structures in grain boundaries. Deep level emission peak (~ 500 nm) which corresponds to oxygen vacancies becomes more intense. The higher Ga doping distorts the film crystallinity where possibility of oxygen vacancies is envisaged [7].

3.3. Sensing response characteristics

UV-response characteristics of the pure ZnO and GZO thin film photodetectors were investigated towards UV radiation of $\lambda = 365$ nm and intensity = 24 $\mu$Watt/cm$^2$ at a bias voltage of 5 V. Figure 6 represents the time-dependent on/off photoconduction measurements carried out for ZnO and GZO thin film samples. It may be seen that when the UV radiation is off, both the prepared UV-photodetectors show a low current ($I_{off}$) which increases and saturates at a particular level in the presence of UV radiation giving $I_{on}$. 

![Room temperature PL Spectra of Pure ZnO and GZO thin films.](image1)

**Fig5.** Room temperature PL Spectra of Pure ZnO and GZO thin films.

![Transient photoresponse of pure ZnO and GZO thin film based UV photodetectors in the absence and presence of UV illumination of 24$\mu$Watt/cm$^2$.](image2)

**Fig6.** Transient photoresponse of pure ZnO and GZO thin film based UV photodetectors in the absence and presence of UV illumination of 24$\mu$Watt/cm$^2$. 
In the absence of UV illumination, the current decreases slowly to attain initial value of current showing persistence. Values of $I_{\text{off}}$, $I_{\text{on}}$, $K$, rise time ($T_r$) and fall time ($T_f$) obtained for both the samples are summarized in Table I. It may be seen from Table I that the $I_{\text{off}}$ for pure ZnO UV photodetector at an applied bias of 5 V is found to be 0.82 $\mu$A and upon UV illumination (24 $\mu$Watt/cm$^2$ intensity) $I_{\text{on}}$ increases to 0.04 mA. When Ga is incorporated into ZnO lattice, a decrease in the $I_{\text{off}}$ is obtained (0.11 $\mu$A) and upon UV illumination $I_{\text{on}}$ increases to 0.1 mA thus giving a very high photoconductive gain of $9.32 \times 10^2$. Variation of $I_{\text{off}}$, $I_{\text{on}}$ and $K$ of both of the photodetectors has been plotted and shown in fig. 7. Rise time has been calculated as the time taken for the dark current to rise to 90 % of saturation value under UV illumination, and recovery time has been taken as the time taken for the photo current to fall to 10 % of the saturation value when UV light is switched off. Variation of $T_r$ and $T_f$ of both of the photodetectors has also been plotted and shown in fig. 8. Rise time and fall time for pure ZnO thin film based photodetector have been calculated to be 6 s and 18 s respectively. The photoresponse obtained for pure ZnO thin film shows persistence and does not return back to its original value. On the contrary, GZO thin film based photodetector exhibits a faster rise and fall time of 3s and 9s respectively.

Table I: Sensing response parameters of prepared UV detectors [Dark current ($I_{\text{off}}$), Photocurrent ($I_{\text{on}}$), Photoconductive Gain ($K$), Rise Time ($T_r$) and Fall time ($T_f$)]

| Sample Prepared | Dark current ($I_{\text{off}}$) $\mu$A | Photocurrent ($I_{\text{on}}$) mA | Photoconductive Gain ($K$) | Rise time ($T_r$) s | Fall time ($T_f$) s |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Pure ZnO       | 0.82            | 0.04            | $4.9 \times 10^1$ | 6               | 18              |
| GZO            | 0.11            | 0.1             | $9.32 \times 10^2$ | 3               | 9               |

Photoconductivity in ZnO thin film can be explained on the basis of adsorption and desorption of oxygen molecules on ZnO thin film surface. Adsorbed oxygen molecules on ZnO surface capture free electrons leading to surface depletion and band bending towards the ZnO surface. Electron hole pairs are generated upon UV illumination, photogenerated holes move along bending and these migrated holes get trapped by negatively charged oxygen molecules reducing the barrier height. Increased conductivity of ZnO on UV illumination is mainly due to the enhanced carrier density and reduced barrier height [14].

On substitution of Ga$^{3+}$ ions at Zn$^{2+}$ sites, density of free charge carriers increase as seen from PL spectra of GZO thin film and it is expected that resistivity should decrease. However, heavy doping of gallium (5.5 %) in ZnO lattice results in creation of some neutral defects which do not contribute towards the conductivity. In spite of the fact that number of free
charge carriers has increased after substituting Ga$^{3+}$ ions with Zn$^{2+}$ ions, a decrease in I$_{off}$ (0.11 $\mu$A) of GZO film has been observed. It is mainly due to the formation of surplus amount of neutral atoms at grain boundaries resulting in enhanced adsorption of oxygen on photodetector surface which is responsible for higher resistance or low conductivity of GZO film and hence low $I_{off}$ [7,15]. On UV exposure, the release of trapped electrons from surface defects or adsorbed oxygen results in the enhanced $I_{on}$ and hence higher value of $K$ is obtained.

Variation of rise time and fall time for both of the photodetectors (ZnO and GZO) is plotted in Fig. 9. After doping of Ga in ZnO thin film, a significant change in the rise and fall time has been observed (Table I, Fig. 9). Rise time (during response cycle) and fall time (during recovery cycle) of GZO thin film UV photodetector has decreased to 3 s and 9 s respectively compared to the values obtained for ZnO thin film photodetector. Hence it can be concluded that GZO thin film photodetector exhibits enhanced photoresponse characteristics towards UV radiations.

![Variation of rise time and fall time for both of the photodetectors (ZnO and GZO)](image)

### 4. CONCLUSIONS

The Ga doped ZnO UV photodetector (GZO) with 5.5 at wt% Ga doping prepared by Sol-gel technique exhibits enhanced photoresponse and less persistence behavior towards UV radiations of $\lambda = 365$ nm and intensity = 24 $\mu$wat/cm$^2$ when biased at 5 volts. The value of photoconductive gain for GZO thin film is found to be about one order higher (9.32×10$^2$) compared to its corresponding value obtained for pure ZnO thin film based photodetector (4.9×10$^1$). Formation of excess neutral atoms in grain boundaries of ZnO after incorporation of very high amount of Ga is found to be responsible for lowering of dark current which results in an enhanced photo response. Doping of gallium in ZnO has also improved the rise time and fall time of the detector which is making GZO photodetector suitable and attractive for fast UV detection. The results are encouraging for the fabrication of a UV photodetector using a simple fabrication technique.

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