



High Quality P -Type Mg-Doped β -Ga₂O_{3- δ} Films for Solar-Blind Photodetectors

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Abstract—The $(\bar{2}01)$ -oriented Mg-doped β -Ga₂O_{3- δ} films were grown on (0001)-sapphire substrates by pulsed laser deposition (PLD) at various oxygen partial pressures ($P_O = 10$ –40 mTorr). The conductivity type of the as-deposited Mg-doped β -Ga₂O_{3- δ} films is proved to be p -type according to the transfer characteristic curves of a top-gate field effect transistor (FET) and rectification curves of the Mg-doped/undoped β -Ga₂O_{3- δ} junction. In addition, the two-terminal solar-blind photodetectors based on Mg-doped β -Ga₂O_{3- δ} films prepared at $P_O = 30$ mTorr exhibit a good optoelectrical performance with a low dark current of 0.19 pA at 10 V, a high $I_{254\text{nm}}/I_{\text{dark}}$ ratio of 1.3×10^4 , fast rise ($\tau_{r1} = 0.035$ s and $\tau_{r2} = 0.241$ s) and decay ($\tau_{d1} = 0.022$ s and $\tau_{d2} = 0.238$ s) times. The present work indicates that the p -type Mg-doped β -Ga₂O_{3- δ} films can be used in the third-generation ultraviolet photodetectors.

Index Terms—Solar-blind photodetectors, wide bandgap, p -type Ga₂O_{3- δ} films, pulsed laser deposition.

I. INTRODUCTION

As a representatives of the third-generation semiconductors, gallium oxide (Ga₂O₃) has five polymorphs: α , β , γ , δ , and ϵ [1]–[5]. Among them, β -Ga₂O₃ is the most stable phase with an intrinsic wide bandgap, high transmittance in

the ultraviolet (UV)-visible-near infrared (NIR) region [6]–[8]. Therefore, it can be widely used in high power devices, UV photodetectors, photoluminescence devices, gas sensors, etc [9]–[14]. It should be emphasized that it is suitable for the application of solar-blind photodetectors ($\lambda \leq 280$ nm) since β -Ga₂O₃ has an ultra-wide optical bandgap of about 4.9 eV (253 nm), effectively shielding the influence caused by solar radiation and artificial light sources [15]–[17].

Many efforts have been made to realize p -type Ga₂O₃ by doping N, Se, Zn, and Mg elements as acceptor dopants for the applications of optoelectronic and power devices [19]–[26]. Recently, Wu *et al.* grew p -type N-doped β -Ga₂O₃ films with Hall hole mobility of $23.6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and hole concentration of $1.56 \times 10^{16} \text{ cm}^{-3}$ for the application of optoelectronic devices [19]. Moreover, the p -type Zn-doped β -Ga₂O₃ ultra-wild semiconductors have a higher critical breakdown field (13.2 MV/cm) than SiC (3 MV/cm), GaN (3.3 MV/cm), β -Ga₂O₃ (~ 8 MV/cm), and diamond (10 MV/cm) for the application of power electronics [24]. However, it is still a big challenge to achieve a good p -type conductivity and stability for the third-generation semiconductor β -Ga₂O₃ due to the strong hole-trapping effect, large acceptor ionization energy, self-compensation effect, and low hole mobility.

Among the acceptors, Mg is predicted to be the most promising candidates of p -type Ga₂O₃ due to the lowest formation energy and a relatively shallow acceptor level [25]–[27]. Qian *et al.* obtained weak p -type Ga₂O₃ thin films by doping Mg, and their photodetectors have a low dark current (4.1 pA at 10 V), high response (23.8 mA/W), and short decay time (0.02 s) under 254 nm UV light for the solar-blind photodetectors [26]. While the resistance of Mg-doped β -Ga₂O₃ will be high since Mg serves as compensating acceptors. In addition, the film phase will become ϵ from β with increasing the Mg concentration [28]. It is difficult to obtain stable p -type Mg-doped Ga₂O₃ with a good conductivity because of the deep level acceptor and self-compensating effect [29]. Fortunately, the pulsed laser deposition (PLD) can be used to prepare p -type Mg-doped Ga₂O₃ films at a high deposition temperature and oxygen pressure by inducing oxygen vacancy concentration [30].

In the letter, the crystalline structure, composition, optical response, and optoelectrical properties of the Mg-doped β -Ga₂O_{3- δ} films prepared by PLD were systematically investigated. It has been found that the present films have a $(\bar{2}01)$ -preferred orientation with p -type behavior. Moreover, the p -type Mg-doped β -Ga₂O_{3- δ} films have a

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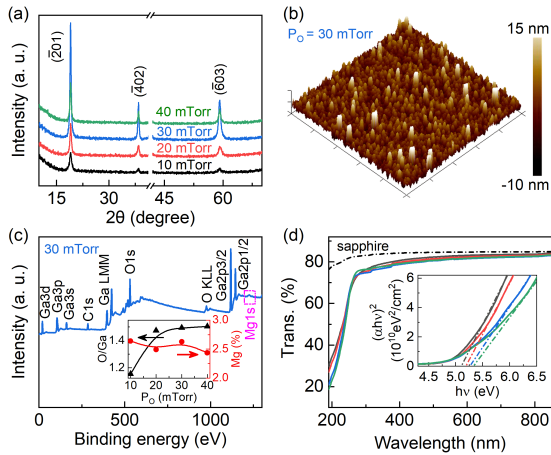


Fig. 1. (a) XRD of the Mg-doped Ga₂O_{3- δ} films deposited at $P_O = 10, 20, 30,$ and 40 mTorr. (b) The AFM image with a scanning range of $5 \mu\text{m} \times 5 \mu\text{m}$ and (c) full XPS spectrum of the Mg-doped Ga₂O_{3- δ} films deposited at $P_O = 30$ mTorr. Inset: O/Ga and Mg concentration as a function of oxygen partial pressure (P_O). (d) Transmittance as well as the $(\alpha h\nu)^2$ vs. $h\nu$ (inset) spectra of Mg-doped Ga₂O_{3- δ} films.

good optoelectronic performance under the UV illumination (254 nm) for solar-blind photodetectors.

II. EXPERIMENTAL

The Mg-doped β -Ga₂O_{3- δ} films were deposited on (0001)-sapphire substrates by the PLD method using a 3% Mg-doped Ga₂O₃ target. The film deposition temperature is 700 °C, and the oxygen partial pressure (P_O) is various from 10 to 40 mTorr. Moreover, the top-gate field effect transistors (FETs) and Mg-doped/undoped Ga₂O_{3- δ} junctions have been fabricated to detect the conductivity type of the as-deposited films. Finally, two-terminal Mg-doped β -Ga₂O_{3- δ} based photodetectors have been fabricated.

The crystalline structure, surface morphology, and composition of Mg-doped β -Ga₂O_{3- δ} films were analyzed by X-ray diffraction (XRD), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The double-beam ultraviolet-infrared spectrophotometer was used to measure the film transmittance in the wavelength range of 190–850 nm. The optoelectrical performance of β -Ga₂O_{3- δ} based devices were measured by an accurate semiconductor parameter analyzer Keithley 4200-SCS. A UV quartz tube with a pure UV filter was used as the UV light source (254 nm) to probe the photoelectric behavior of solar-blind photodetectors.

III. RESULTS AND DISCUSSION

In Fig. 1a, the XRD curve feature clearly agrees with the XRD standard card (JCPDS Card: No. 43-1012). There are three peaks nearby 18.9, 38.4, and 59.1°, corresponding to the (201), (402), and (603) crystal planes of β -Ga₂O₃ with no impurity phase [26]. It indicates that Mg²⁺ ions are incorporated into the β -Ga₂O₃ structure by replacing Ga³⁺ ions [26]. The as-deposited films with the (201)-orientation are polycrystalline. According to the Scherrer's equation [32], the average grain size of the films deposited under $P_O = 10, 20, 30,$ and 40 mTorr are 24.6, 34.3, 36.8, and 35.1 nm, respectively. The Mg-doped Ga₂O_{3- δ} films ($P_O = 30$ mTorr)

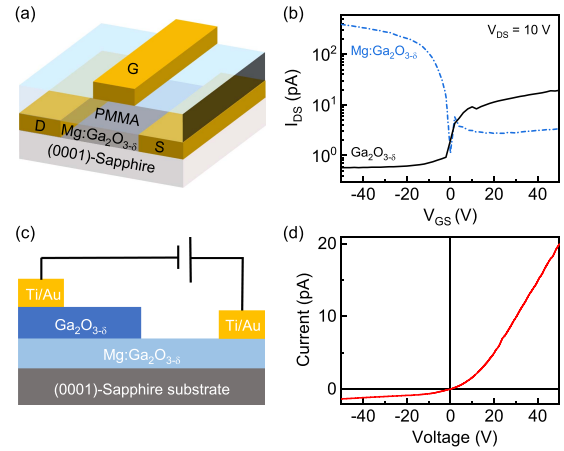


Fig. 2. (a) Schematic diagram and (b) transfer characteristic curves of the β -Ga₂O_{3- δ} based FETs. (c) Schematic diagram and (d) I-V characteristics of the Mg-doped/undoped β -Ga₂O_{3- δ} p-n junction.

has the largest grain size due to the changes of kinetic energy and mean free path of plasma plume, which is consistent with the results of AFM images (cf., Fig. 1b).

In Fig. 1c, the XPS spectrum of a Mg-doped Ga₂O_{3- δ} film ($P_O = 30$ mTorr) reveals that the as-deposited films have a Mg concentration of around 2.5%. The O/Ga ratio values of the films deposited under $P_O = 10, 20, 30,$ and 40 mTorr are about 1.15, 1.47, 1.49, and 1.50, respectively. It means the oxygen vacancies in the films are reduced by increasing the oxygen partial pressure. The transmission spectra show that the transmittance exceeds 80% in the near UV-visible-NIR region, and the absorption edge appears at about 270 nm (cf., Fig. 1d). Note that the absolute average transmittances of the Mg-doped β -Ga₂O_{3- δ} films will exceed 90% in the transparent region after deducting the influence of sapphire substrates. The optical bandgap of the Mg-doped Ga₂O_{3- δ} films prepared at $P_O = 30$ mTorr is about 5.2 eV (238.5 nm) based on the Tauc's relationship [32], as illustrated in the inset of Fig. 1d. It indicates that the present films can be applied in UV photodetectors.

A further step, the conductivity type of the Mg-doped β -Ga₂O_{3- δ} films has been investigated based on the transfer curves of related FETs (cf., Figs. 2a and 2b). For comparison, pure β -Ga₂O_{3- δ} based FETs were prepared under the same conditions. As the gate voltage (V_{GS}) is swept from -60 to $+60$ V, there is a process from depletion to accumulation, which indicates that the conductivity type of the pure β -Ga₂O_{3- δ} films is *n*-type. On the contrary, the transfer response of the Mg-doped β -Ga₂O_{3- δ} based FETs reveals that the conductivity type of the Mg-doped β -Ga₂O_{3- δ} films is *p*-type. Furthermore, the Mg-doped/undoped β -Ga₂O_{3- δ} junctions were fabricated, as illustrated in Fig. 2c. In Fig. 2d, the I-V characteristics of the junctions exhibit a typical rectification characteristic with a rectification ratio of 30.9 ± 20 V, which confirms that the as-deposited Mg-doped β -Ga₂O_{3- δ} films have *p*-type behavior.

The two-terminal solar-blind photodetectors based on the as-deposited films were fabricated by evaporating 2nm/60nm-thick Ti/Au electrodes to characterize the photoelectric properties of the *p*-type β -Ga₂O_{3- δ} films (cf., Fig. 3a).

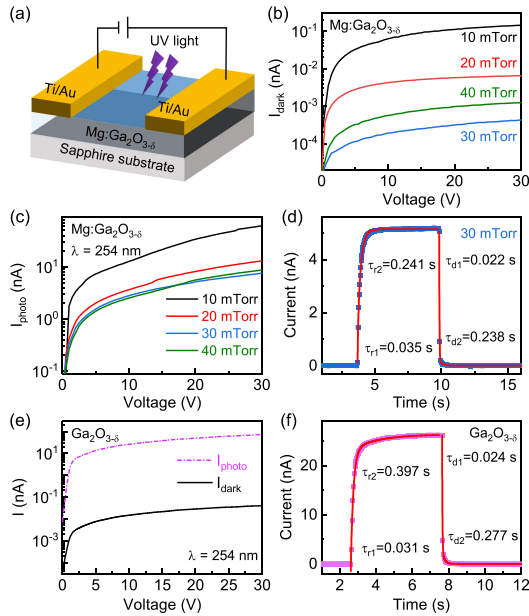


Fig. 3. (a) Schematic diagram, (b) $I_{\text{dark}}-V$, (c) $I_{\text{photo}}-V$ at $\lambda = 254$ nm and (d) $I-t$ curve of the two-terminal solar-blind Mg-doped $\beta\text{-Ga}_2\text{O}_{3-\delta}$ based photodetector by applying a single pulsed light at $V_{\text{app}} = 10$ V. (e) $I-V$ and (f) $I-t$ curves of the undoped $\beta\text{-Ga}_2\text{O}_{3-\delta}$ based photodetector.

In Fig. 3b, the Mg-doped $\beta\text{-Ga}_2\text{O}_{3-\delta}$ films grown under $P_{\text{O}} = 30$ mTorr have the lowest dark current (I_{dark}) due to the ideal O/Ga ratio and large grain size, that is, the decrease of oxygen vacancies results in a reduction of carriers. Fig. 3c shows that the photocurrent ($I_{254\text{nm}}$) is almost unchanged for the devices ($P_{\text{O}} = 20, 30,$ and 40 mTorr). For the case of $P_{\text{O}} = 10$ mTorr, small grain size and more oxygen vacancies result in a large photocurrent [33]. Note that the I_{dark} and I_{photo} responses suggest that the resistance of Mg-doped Ga_2O_3 films is higher than other p -type Ga_2O_3 (e.g. $\text{Zn:Ga}_2\text{O}_3$) due to the overcompensation by oxygen vacancies [34], [35].

The time-dependent photoelectric response tests were carried out by applying a bias voltage (V_{app}) of 10 V, as shown in Fig. 3d. The photocurrent curves have been fitted by the relationship [33]: $I = I_0 + Ae^{-t/\tau_1} + Be^{-t/\tau_2}$. Here, I_0 is the steady-state photocurrent, A and B are fitting parameters, and τ_1 and τ_2 are the relaxation times of the fast and slow response parts of the rise or decay edges, respectively. The fast response part is related to the change of photo-generated carriers, which is determined by the film quality. The slow one is related to the trapped or de-trapped process of carriers. The photodetectors based on the Mg-doped $\beta\text{-Ga}_2\text{O}_{3-\delta}$ films ($P_{\text{O}} = 30$ mTorr) have the fastest response speed with rise ($\tau_{r1} = 0.035 \pm 0.004$ s and $\tau_{r2} = 0.241 \pm 0.003$ s) and decay ($\tau_{d1} = 0.022 \pm 0.002$ s and $\tau_{d2} = 0.238 \pm 0.001$ s) times since the carriers are more difficult to be captured in the high quality films with fewer oxygen vacancies. Compare to the optoelectrical performance of the pure $\beta\text{-Ga}_2\text{O}_{3-\delta}$ based photodetectors (Figs. 3e and 3f), the Mg-doped $\beta\text{-Ga}_2\text{O}_{3-\delta}$ based photodetectors have a smaller I_{dark} , larger $I_{\text{photo}}/I_{\text{dark}}$ ratio, and a faster slow-response (τ_{r2} and τ_{d2}) due to the fewer oxygen vacancies.

To further illustrate the optoelectrical performance of Mg-doped $\beta\text{-Ga}_2\text{O}_{3-\delta}$ based solar-blind photodetectors, the device responsivity (R) has been studied, which is defined as

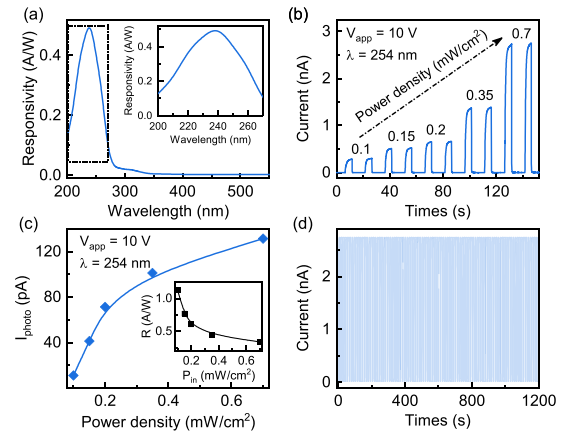


Fig. 4. (a) Response spectra of the photodetectors based on the Mg-doped $\beta\text{-Ga}_2\text{O}_{3-\delta}$ film ($P_{\text{O}} = 30$ mTorr) as a function of illumination wavelength. (b) $I_{\text{photo}}-t$ at different pulsed light power densities. (c) Photocurrent and responsivity (R) of the two-terminal photodetectors as a function of light power density (P_{in}). (d) Dynamic response of the Mg-doped $\text{Ga}_2\text{O}_{3-\delta}$ based solar-blind photodetectors under on/off modulated UV light (254 nm, 0.7 mW/cm²).

$R = I_{\text{photo}}/(P_{\text{in}} \times S)$. Here, I_{photo} is the photocurrent, P_{in} is the power density of the incident light, and S is the effective working area of the device [17]. As a solar-blind photodetector, the response spectra are shown in Fig. 4a. It reveals that the device response wavelength range is about 200-270 nm, which is consistent with the optical bandgap E_g derived from the transmittance spectra (cf., Fig. 1d). Fig. 4b shows that the photocurrent increases with increasing the power density of the incident UV light (254 nm) due to the more photogenerated carriers. The photodetector responsivity (R) decreases with increasing the light power density since the photocurrent becomes saturated (cf., Fig. 4c). In Fig. 4d, a stability test were carried out by applying a voltage of $V_{\text{app}} = 10$ V and UV pulsed light (254 nm, 0.7 mW/cm², and more than 50 periods), which indicates that the present photodetectors have good stability and repeatability.

IV. CONCLUSION

In summary, p -type Mg-doped $\beta\text{-Ga}_2\text{O}_{3-\delta}$ films with the $(\bar{2}01)$ -orientation have been deposited on (0001) -sapphire substrates under various oxygen partial pressures ($P_{\text{O}} = 10\text{--}40$ mTorr) and the optimum pressure is 30 mTorr. A further step, the conductivity type of Mg-doped $\beta\text{-Ga}_2\text{O}_{3-\delta}$ films is proved to be p -type obtained from the Mg-doped $\beta\text{-Ga}_2\text{O}_{3-\delta}$ based FETs and Mg-doped/undoped $\beta\text{-Ga}_2\text{O}_{3-\delta}$ junctions. Furthermore, it has been found that the photodetectors based on the Mg-doped $\beta\text{-Ga}_2\text{O}_{3-\delta}$ films ($P_{\text{O}} = 30$ mTorr) exhibit the optimum optoelectrical performance with a low dark current of 0.19 pA at 10 V, a high $I_{254\text{nm}}/I_{\text{dark}}$ ratio of 1.3×10^4 , fast rise ($\tau_{r1} = 0.035 \pm 0.004$ s and $\tau_{r2} = 0.241 \pm 0.003$ s) and decay ($\tau_{d1} = 0.022 \pm 0.002$ s and $\tau_{d2} = 0.238 \pm 0.001$ s) times, which exhibit good stability and repeatability.

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