Robust Stability of Optical and Electronic Properties of Gallium-Doped Zinc Oxide Thin Films to Gamma Ray Irradiation

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Through combined measurements of broadband optical spectroscopy (10 meV to 6 eV), electrical resistivity, and Hall effect, the effects of gamma ray irradiation on electronic and optical properties of gallium-doped ZnO (GZO) thin films, deposited by ion plating direct-current arc discharge, are investigated. A significant number of films, deposited at various discharge currents (I_D = 100–200 A) and oxygen gas flow rates (OFR = 0–25 sccm), exposed to doses of 15 and 30 kGy of gamma rays, are studied. The results indicate strong resilience of films to irradiation: visible range transparency is reduced by 10–12% and the optical bandgap shifts to lower energies by less than 3%, while electrical resistivity, carrier concentration, and electron mobility remain nearly unchanged.

1. Introduction

Gallium- and aluminum-doped ZnO (GZO and AZO) provide a low-cost alternative to the extensively used indium oxide-based transparent conductors for various technological applications, such as photovoltaic devices, touch screen technology, and transparent and flexible electronics.[1,2] While AZO is particularly attractive because of the natural abundance and lower cost of aluminum, when compared to gallium, the ion radius of Ga^{3+} matches better than that of Zn^{+2}, and the doping with Ga results in a lower electron effective mass, thereby allowing for higher mobility in GZO films.[3] In addition, recent reports have demonstrated their potential to be used for ultraviolet (UV) detectors and solar cell integrated transparent antenna, motivating further the interest in the GZO compound.[4,5] High carrier concentrations ($\approx 1 \times 10^{21}\,\text{cm}^{-3}$), low resistivity ($\approx 2 \times 10^{-4}\,\Omega\cdot\text{cm}$), and high electron mobility ($\approx 20\,\text{cm}^2\,\text{V}\cdot\text{s}^{-1}$) have been reported in GZO films obtained by various methods.[6–9] Among them, ion plating direct-current arc discharge has been particularly successful, where carrier concentrations exceeding $1 \times 10^{21}\,\text{cm}^{-3}$ and mobility of the order of $30\,\text{cm}^2\,\text{Vs}^{-1}$ were reported.[8,9]

The possibility of using GZO thin films as transparent electrical contacts on solar cells opens further potential applications in space technology. However, for such prospective, one has to assess the performance of films under the exposure to radiation present in space.[10,11] In this work, we report the effects of highly energetic radiation, gamma rays, and electrical and optical properties of GZO thin films. We discuss the changes in optical bandgap, visible range transparency, electrical resistivity, mobility, and carrier concentration under irradiation.

2. Experimental Section

GZO films of 2000 Å thickness were deposited on glass substrate by ion plating direct-current arc discharge, as described in the previous study.[9] While there was no critical reason for the choice of film thickness, this value would be suitable for the use of GZO films as transparent electrodes,[1] providing high visible transparency and high electrical conductivity at the same time, as we will demonstrate in the following section. We measured more than ten as-deposited samples grown at various discharge currents I_D between 100 and 200 A, and oxygen-flow rates (OFR) between 0 and 25 sccm, all of them showing the same behavior. Herein, we present data on three samples with high carrier concentration, around $1 \times 10^{21}\,\text{cm}^{-3}$.

The irradiation was performed at IRASM Center from the Horia Hulubei National Institute of Physics and Nuclear

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Engineering (IFIN-HH), using a commercial Co 60 gamma source, which ensures uniform irradiation over large areas/volumes.

Optical reflectance in the range of 0.200–124 μm (10 meV–6 eV) and transmittance between 0.200 and 0.900 μm were measured using a combination of two spectrometers: a Bruker Vertex 70 Fourier-transform infrared spectrometer (0.4–124 μm) and a Perkin-Elmer 650 UV/VIS grating spectrometer (0.2–0.9 μm). Reflectance was measured against both gold and aluminum references for accurate determination of its magnitude, especially important in the long-wavelength regime. Four-probe resistivity and Hall effect were measured by means of Van der Pauw method, using a commercial system from NanoMagnetics Instruments.

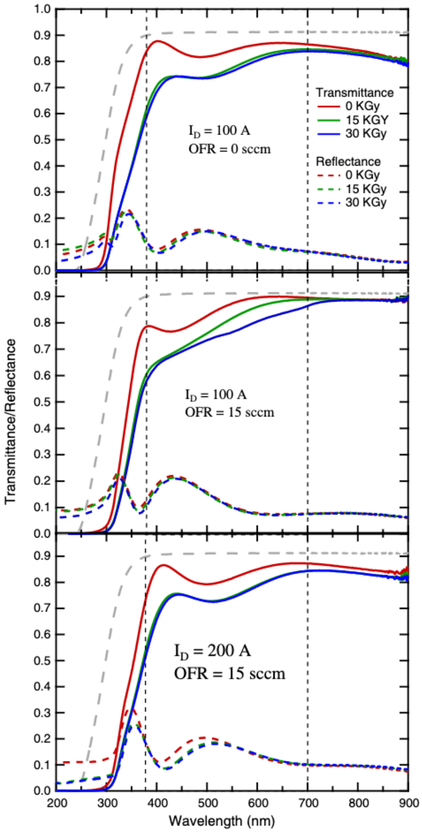

Figure 1. Optical reflectance and transmittance of as-deposited and gamma ray irradiated GZO thin films, from UV to near-infrared range. Vertical discontinuous lines mark the visible region.

3. Results

Figure 1 shows transmittance and reflectance from UV to near-infrared (200–900 nm), for both as-deposited and irradiated GZO films, deposited in three different conditions, as explained in each of the graph captions. All films are highly transparent in the visible range (over 80% transmittance), with a sharp absorption edge associated with an optical bandgap in the UV spectral region. Reflectance is about 20% or lower, indicating that the films have very low absorption in the visible range. These results are in good agreement with previous reports on samples obtained in the same conditions.[9]

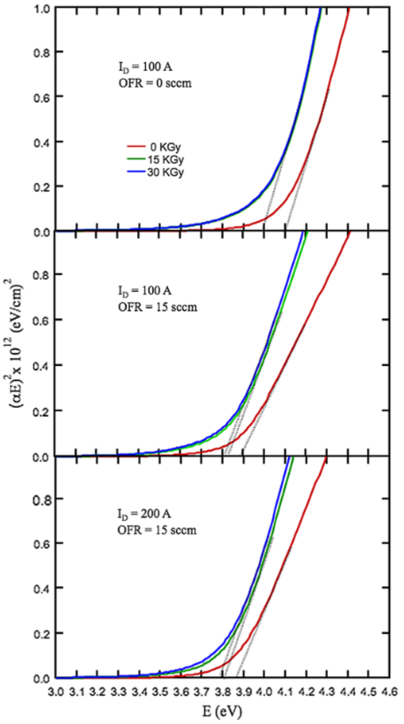

Figure 2. Tauc plots of absorption for both as-deposited and gamma ray irradiated GZO thin films. The dashed lines are extrapolations used to indicate the optical gap.

Table 1. Electrical and Hall data for as-deposited and irradiated GZO films.

Sample	Irradiation [kGy]	ρ [Ω·cm]	n_e [cm^{-3}]	μ [cm^2 V·s]
	0	1.93×10^{-4}	1.51×10^{21}	21.4
$I_D = 100$ A	15	1.85×10^{-4}	1.47×10^{21}	22.9
OFR = 0 sccm	30	1.86×10^{-4}	1.49×10^{21}	22.5
	0	3.07×10^{-4}	0.9×10^{21}	21.8
$I_D = 100$ A	15	3.37×10^{-4}	0.8×10^{21}	22.5
OFR = 15 sccm	30	3.43×10^{-4}	0.9×10^{21}	20.3
	0	2.95×10^{-4}	1.0×10^{21}	20.6
$I_D = 200$ A	15	2.98×10^{-4}	0.9×10^{21}	22.5
OFR = 15 sccm	30	3.04×10^{-4}	1.0×10^{21}	20.4

Herein, we look at the effects of gamma ray irradiation on optical properties. We observed that overall, the visible range transmittance is reduced by about 10–12%, and the absorption edge shifts very slightly to lower energy. Along with the observation that the visible range reflectance remains almost unchanged, we suggest that the main effects of irradiation are to slightly increase absorption and to reduce the optical band gap.

To better illustrate these effects of irradiation, we first calculate the absorption coefficient from measured reflectance (R) and transmittance (T)

$$\alpha = \frac{1}{d}\ln\left(\frac{1-R}{T}\right) \tag{1}$$

where d represents the film thickness. Then, following a common practice in estimating the bandgap in transparent conductive oxides,[6,9,12–14] in **Figure 2**, we plot $(\alpha E)^2$ versus energy (E), according to the following Tauc relation, and determine the optical gap E_g as the intercept of the plots[15]

$$\alpha E = (E - E_g)^{1/2} \tag{2}$$

As it can be seen from Figure 2, the optical bandgap in our samples is close to 4 eV, in good agreement with previous measurements[9] and among the highest values reported in the literature for GZO thin films. The larger bandgap values are indicative of higher carrier concentration, as we will discuss later. From the extrapolations shown in Figure 2, we calculate that with irradiation, the gap shifts to lower energy, but by less than 3%. It remains significantly above 3.1 eV, the higher energy limit of the visible spectrum. We also note from Figure 1 and 2 a very consistent trend with irradiation dose. Most changes occur up to 15 kGy, without much effect after doubling the dose to 30 kGy. Further studies, both at lower and higher doses, as well as complementary crystallographic and analytical measurements, will help better understand the origins of this behavior.[16]

The effects of gamma rays on electrical properties of GZO thin films are summarized in **Table 1**. The relatively large carrier concentration $n_e \approx 1 \times 10^{21}$ cm^{-3} indicates large Fermi energy, shifting the onset of optical transition between valence and conduction bands to higher energies, according to the Burstein-Moss model for doped semiconductors[17,18] and justifying the large optical bandgap measured in Figure 2. The main conclusion from Table 1 is that electrical properties (dc-resistivity, mobility, and scattering rate) remain basically unchanged by irradiation.

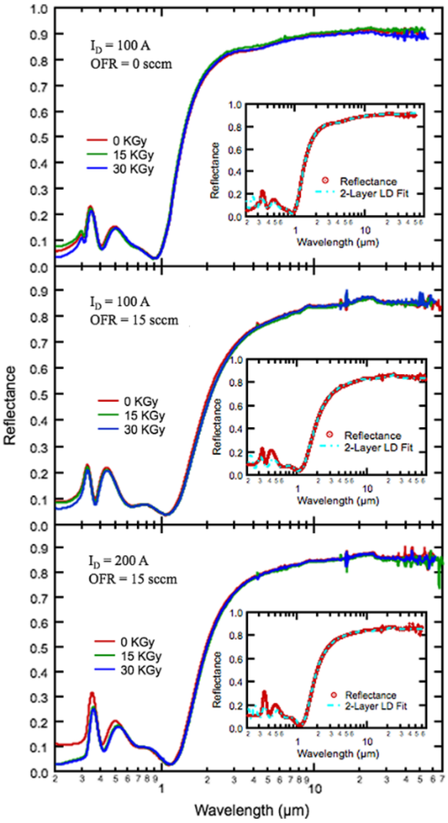

Figure 3. Broadband reflectance of as-deposited and irradiated GZO thin films. The insets show a two-layer model fit, as explained in the main text.

To further verify such findings, we plot in **Figure 3** the broadband reflectance, including the low energies (long wavelengths) spectral region, where the response to electromagnetic radiation is dominated by the free (conduction) carriers.

Reflectance in the limit $\lambda \to \infty$ ($E \to 0$) is about 90%, and a clear Drude (free carrier) plasma edge can be distinguished for all samples. From reflectance alone, one can see that neither low energy value nor the position of the plasma edge is affected by irradiation. Extraction of the free carrier parameters (Drude plasma frequency, scattering rate, and dc-conductivity) of the GZO films alone from the measurements in Figure 3 is complicated by the contribution of the substrate as well. One can observe that even in the region where reflectance is as high as almost 90%, there are some sharp features which are phonons of the glass substrate. To extract the parameters of the films alone, we involve a two-layer model, assuming a Lorentz–Drude (LD) behavior for each layer, substrate and film, respectively.[19,20] The substrate was measured and fit separately, and its parameters were then fixed when fitting the film/substrate system. This way, we disentangled the properties of the film from those of the substrate. Details and more examples on as-deposited samples are provided in our previous study,[10] and in the inset of Figure 3, we show an example of two-layer model fit of the as-deposited samples from each batch. The fits very well reproduce the experimental data at long wavelength, in the region dominated by the free carrier response, and the discrepancy at short λ is mainly due to absorption across the bandgap, which was not factored in our model. Focusing on the Drude parameters, for one sample ($I_D = 200$ A, OFR = 15 sccm), we obtained plasma frequency ($\omega_p^2 = n_e e^2/m^* \varepsilon_0$) and the scattering rate $1/\tau$ values of 1.75 and 0.14 eV, respectively. In contrast, if these parameters are calculated from the resistivity and Hall data from Table 1, taking the effective mass $m^* = 0.35$ (based on the previous study[9]), the values would be $\omega_p = 1.88$eV and $1/\tau = 0.14$eV, in excellent agreement with the results from optical reflectance mentioned earlier. In fact, we found that optical and electrical transport measurements agree within better than 10%, which is about the uncertainty of our LD fit, for all samples.

When comparing the parameters of the as-deposited with those of the irradiated films, we found almost identical values, similar to those observed in dc-transport measurements (Table 1). Therefore, optical reflectance data further confirms the stability of electrical properties under gamma-ray irradiation with doses up to 30 kGy. The fact that the carrier concentration in particular is not affected by irradiation suggests that shift to lower energy of the absorption gap, observed in Figures 1 and 2, is not due to a reduction in Fermi energy, according to the Burstein-Moss model, but has rather different origins. It is possible that radiation produces structural changes in the lattice parameters, hence ionic radii, which affect the size of the bandgap of ZnO itself. Such possibility is worth investigating, using crystal structure tools.

4. Conclusions

Using combined measurements of broadband spectroscopy, resistivity, and Hall effect, we have demonstrated the stability of the optical and electronic properties of GZO thin films to gamma-ray irradiation up to 30 kGy. The optical bandgap shifts to lower energies by less than 3%, visible range transparency is reduced by about 10%, and the electronic properties, such as resistivity, carrier concentration, scattering rate, and mobility, remain nearly unchanged. While complementary studies are required to understand the reasons for such behavior, our findings demonstrate remarkable potential for the use of GZO films in space technology or other environment where radiation is present. Further studies, to assess the effects of ion irradiation, which is also present in space environment, are being planned.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

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