# Ga-Doped IZO Films Obtained by Magnetron Sputtering as Transparent Conductors for Visible and Solar Applications

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## Abstract

C-axis textured thin films of gallium-doped indium zinc oxide (GIZO) with a 2% ratio of Ga/Zn, were obtained via RF-magnetron sputtering with high transparency and electrical conductivity. A Box-Behnken response surface design was used to evaluate the effects of the deposition parameters ($In_2O_3$ target power, deposition time, and substrate temperature) on the chemical composition, optical, electrical, and structural properties of the GIZO films. The optical constants and the electrical properties were obtained using optical models. The GIZO stoichiometry, and therefore the In/Zn atomic ratio, affected the crystallinity, crystalline parameters, band gap, and charge carrier mobility of the GIZO films. The charge carrier density was related to the change in the crystalline parameters of the hexagonal structure and the In/Zn atomic ratio. The best electrical conductivity values ($1.75 \times 10^3\ \Omega^{-1}\ cm^{-1}$) were obtained for GIZO films with In/Zn ratio $\geq 1$. Several figures of merit (FOM) defined for the visible and solar regions were comparatively used to select the optimal In/Zn atomic ratio that provided the best balance between the conductivity and the transparency. The optimal In/Zn ratio was in a range of 0.85-0.90 for the GIZO films.

**Keywords:** TCO; GIZO; figure of merit; electrical; optical; solar properties.

## 1. Introduction

Transparent conductive oxides (TCOs) are a very important part in many optoelectronic devices such as solar cells and also in new relevant devices for energy harvesting and storage [1-3] such as photo-supercapacitors, which are novel and promising devices that enable the production of solar energy and its storage in the same device [4, 5]. Obtaining efficient solar cells and photo-supercapacitors requires a careful design of all of its parts. Transparent electrodes play an important role as an active part in the development of these devices. The main advantage of these compounds is that they can be obtained using various methods such as spray pyrolysis [6, 7], electrodeposition [8], or magnetron sputtering [9]. ZnO doped with Ga [10], Al [11], or In [12] are materials that can fulfil the requirements for optoelectronic devices. An opportunity to obtain better TCO materials involves using ZnO compounds doped with Ga and In [13], that is, indium–gallium–zinc oxide (GIZO). When properly doped, zinc atoms are substituted by trivalent atoms ($X^{3+}$, where X = Al, In, and Ga). The extrinsic donors due to dopant are more stable than the intrinsic donors due to their native defects. However, they present a limitation in the improvement of conductivity when increasing the dopant content of Al, Ga, or In above a certain value since the conductivity and transparency decrease. This saturation in the doping of ZnO by Al or Ga is possibly due to the conduction mechanisms in these compounds [14]. There is evidence that saturation in doping with Ga is reached at approximately 2 at% [15, 16]. For higher values of Ga doping, the conductivity decreases, likely due to the degradation of the crystallinity of the film because of the difference in the ionic radius between the $Ga^{3+}$ (0.062 nm) and $Zn^{2+}$ (0.074 nm). The resulting effect would be the loss of charge carrier mobility [17]. Another possible reason would be that the increase in the dopant atoms produces neutral defects that do not contribute to the conductivity. In addition, the neutral atoms can be segregated at the grain boundaries, increasing carriers scattering [18]. The charge carrier density and their mobility determine the conductivity. To obtain significant improvements, it is necessary to combine both adequately. GIZO can improve its optoelectronic properties with respect to Ga:ZnO or Al:ZnO. Kimizuka and Mohri [19] synthesised GIZO for the first time in 1985, and Shunpei Yamazaki [20] discovered that various GIZO crystal morphologies are formed in addition to amorphous and single-crystal morphologies. The discovered c-axis-aligned crystalline GIZO and nanocrystalline GIZO morphologies showed significant differences from single-crystal and polycrystalline structures. Nanocrystalline GIZO (nc-GIZO) exhibited nanometre-sized crystals that were oriented in random directions [21].

The experimental response surface designs, which are the most suitable for the optimisation of one or several responses, are limited to three factors by a principle of economy in the experimental effort. If it is suspected that more than three factors may have significant effects, then it is appropriate to select three of them and fix the rest at a value that is considered adequate. For this reason, and although it was obvious that the variation in the amount of Ga will influence the final properties of GIZO films, it was decided to select three sputtering parameters and the Ga/Zn ratio was set at 2% based on the previous work of our group and other studies found in the literature [9,15]. Therefore, to obtain GIZO films with optimal electrical conductivity and transparency, a Box-Behnken response surface experimental design was used to evaluate the effects of three factors: power applied to the $In_2O_3$ target, substrate temperature, and deposition time. The goal is to establish their influence on GIZO films properties such as charge carrier density, mobility, and crystallinity, among other. To obtain films with a good compromise between transparency and conductivity to be used as transparent electrodes, Haacke [22], Gordon [23] and Hu et al. [24] defined figures of merit (FOMs). In this work, these FOMs have been modified for the visible and solar regions and comparatively applied to the GIZO films to obtain the best compromise between transparency and conductivity.

## 2. Experiment

GIZO electrodes were deposited via RF magnetron sputtering in co-sputtering mode on 1 and 2 $cm^2$ glass substrates after the proper wet-chemical cleaning in ultrasonic baths, isopropanol (10 min), deionised water, and acetone (10 min), and dried under nitrogen flow. Two types of ceramics targets from AJA International were employed: $Ga_2O_3$ (2%) - doped ZnO target (98%) and $In_2O_3$ (99.99%). The 150 W applied power to the Ga:ZnO target was selected on the base of previous studies [9], and the obtained Ga:ZnO film was considered as corresponding to a ratio of zero for the In/Zn ratio.

A Box-Behnken response surface factorial design was used to organise the experiment and identify the effects of three magnetron sputtering parameters such as the $In_2O_3$ target power (P), deposition time (t), and substrate temperature (T) on the properties of the GIZO films and the potential interactions between these three factors. The films were prepared in random order to include unidentified sources of variability in the experimental error. The three levels used for the factors are shown in Table 1. The power applied to the $In_2O_3$ target was 80 W, 110W, and 140 W, at substrate temperatures 150, 250, and 350 ºC, respectively. The films were deposited during 20, 40 and 60 min. The full experimental design is shown in Supplementary Material Table ST1. The working pressure in the vacuum chamber was kept constant at 1.4 x $10^{-2}$ mbar, and a high-purity (5 N) Ar gas stream regulated by a mass flow controller at 12 sccm was used.

**Table 1**: Factors and levels used for the Box-Behnken response surface experimental design and identification of the sample.

| Level (symbolic) | Factor | | |
|---|---|---|---|
| | **$In_2O_3$ applied power (W)** | **Substrate temperature (ºC)** | **Deposition time (min)** |
| -1 | 80 | 150 | 20 |
| 0 | 110 | 250 | 40 |
| +1 | 140 | 350 | 60 |
| Identification of the film: GIZO_ power_temperature_time | | | |

The structural characterisation of the sample was conducted via X-ray diffraction (XRD) using a PANalytical X'Pert PRO MRD diffractometer and a PANalytical PW3050/65 (θ/2θ) goniometer. Identification of the composition of the as-deposited GIZO coatings was accomplished using X-ray diffraction (XRD) in a Bragg-Brentano configuration on a Philips X´Pert PRO MPD with monochromatic high-intensity CuKα radiation (λ¼). The average crystallite size was calculated using the Scherrer equation:

$$D_{hkl} = \frac{K \ \lambda}{\beta_{hkl} \cos\theta_{hkl}}, \tag{1}$$

where $D_{hkl}$ is the crystallite size, λ is the wavelength used (1.54 Å), $\beta_{hkl}$ is the corrected angular line width at half-maximum intensity in radians, $\theta_{hkl}$ is Bragg's angle, and K is the shape factor. The $\beta_{hkl}$ parameter was corrected using the following formula:

$$\beta_{hkl} = \sqrt{\beta_{exp}^2 - \beta_{ins}^2} \ , \tag{2}$$

where $\beta_{exp}$ corresponds to the experimentally determined full width at half of the maximum intensity, FWHM, of the peak. The instrumental width was determined as $\beta_{ins}$ = 0.07º using a standard lanthanum hexaboride ($LaB_6$) powder pattern.

High-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) were achieved with a FEI TALOS F200X microscope operated at 200 kV. Field-emission scanning electron microscopy (FE-SEM) images of the GIZO thin films were obtained on a Helios NanoLab 650 Dual-Beam microscope from FEI. An energy-dispersive spectrometer (EDS) from Oxford SDD Detector was used to obtain the atomic concentration of the In, Ga, and Zn elements in the cross-section of the GIZO thin films. Topographic atomic force microscopy (AFM) examinations were performed using a NanoScope V tapping-mode AFM (Veeco Instruments) employing sharp silicon tips and NanoScope Analysis Software version 1.4 2010 from Bruker. The thickness of the film was obtained via HRTEM, FE-SEM and EDS cross sectional images.

Transmittance and hemispherical reflectance measurements were achieved in the UV–Vis-NIR range (200–2500 nm) using a Cary 5000 spectrometer from Varian with an integrating Spectralon sphere. Visible transmittance and reflectance $T_{vis}$, and $R_{vis}$ respectively, were calculated using Eq. 3

$$T_{vis} = \frac{\int_{370}^{780} D_{65}(\lambda)\, V(\lambda)\, T(\lambda)\, d\lambda}{\int_{370}^{780} D_{65}(\lambda)\, V(\lambda)\, d\lambda}, \qquad (3)$$

where, $D_{65}(\lambda)$ is the spectral power distribution of CIE standard illuminant D65, $V(\lambda)$ is the photopic spectral sensitivity function for human vision [25], and $T(\lambda)$ is the spectral transmittance of the sample, glass/IGZO film. $T(\lambda)$ is substituted by $R(\lambda)$ for visible reflectance.

The solar transmittance and reflectance ($T_{solar}$, and $R_{solar}$, respectively) were calculated using Eq. 4

$$T_{solar} = \frac{\int_{300}^{2500} I_{AM1.5}(\lambda)\, T(\lambda)\, d\lambda}{\int_{300}^{2500} I_{AM1.5}(\lambda) d\lambda}, \qquad (4)$$

where $I_{AM1.5}$ is the standard spectrum distribution of solar energy for 1.5 atmosphere thickness, corresponding to a solar zenith angle of 48.2°. The solar reflectance can be obtained using R(λ) instead of T(λ).

The spectral absorptance is calculated as A(λ)= 1- R(λ)- T(λ), and the solar absorptance $\alpha_{solar}$ as

$$\alpha_{solar} = \frac{\int_{300}^{2500} I_{AM1.5}\left(1-R(\lambda)-T(\lambda)\right) d\lambda}{\int_{300}^{2500} I_{AM1.5}\, d\lambda} \qquad (5)$$

The concentration and oxidation state were studied via X-ray photoelectron spectroscopy (XPS) using an ESCA 5701 from Physical Electronics (PHI). An Mg Kα radiation source (15 eV) with an operating power of 400W in an ultra-high vacuum system with a base pressure of ~$1.3\times10^{-8}$ Pa, was employed.

Sheet resistance $R_{sq}$ and electrical resistivity ρ of the GIZO films were measured in a Hewlett Packard 16055A chamber using a Hewlett-Packard 4140B as DC source and Keithley 181 as nanovoltmeter. The values of the charge carrier density and mobility were calculated using the fitted optical model parameters and the electrical resistivity, and the obtained values were corroborated via experimental Hall effect measurements. The electrical charge carrier density and Hall mobility were assessed by Hall Effect measurement using the four-point van der Pauw method. The measurements were performed from 30 K to 300 K, at a current of 1 mA and 3000 Gauss magnetic field. The system was homemade, and the measurements used a commutator 3488A switch/control unit from Hewlett-Packard, a current and voltage source from Keithley, an electromagnet TCR Power Supply from EM Inc., an 805 Temperature Controller from Lake Shore Cryotronics, and a TPH 055 vacuum system from Balzers Pfeiffer. The software was developed with LabView.

## 3. Results and discussion

### 3. 1 Structural, compositional, and morphological properties of GIZO thin films

From the analysis of the Box-Behnken design, the applied power was the main significant positive effect on the In/Zn atomic ratio, which means that there was a linear dependence, a positive slope, between the $In_2O_3$ target power and the In/Zn ratio [26], as seen in Fig. 1(a). There was also a smaller positive effect of the deposition time on the In/Zn ratio. The Ga/Zn ratio remained near constant with median of 0.021 and standard deviation of $3.7 \times 10^{-3}$ as seen in the values of the atomic Ga/Zn ratio and the Ga/(Zn+In+Ga) shown in table ST2. However, the main significant effect on the thickness was the deposition time. The effect of the applied power on the thickness was less significant. This means, as expected, that the thickness increased linearly with the deposition time as shown in Fig. 1(b), and additionally by the increase in the amount of deposited In. A Pareto graph of the effects for both responses is shown in Supplementary Material Fig. SF1 (a, b).

Fig. 2 shows the XRD diffraction patterns. The GIZO films grew hexagonal c-axis textured with a main diffraction peak around $2\Theta=31°$ corresponding to (0 0 n) crystallographic planes. This peak does not appear at a fixed $2\Theta$ angle because $2\Theta$ changes with the In/Zn ratio. Fig. 2(a-c) shows the XRD patterns for the samples obtained at 80, 110, and 140 W applied to the $In_2O_3$ target. Increasing the power increased the In/Zn ratio, and the crystal size of the films decreased with the increasing In/Zn atomic ratio (Fig. 3). It has been reported that crystalline films are generally obtained at low In/Zn atomic ratios. When In/Zn is higher, amorphous films are obtained [27]. The amorphisation in the In-rich IZO films was probably because the In atoms would locate in or near the grain boundary regions [28, 29]. This could also be attributed to the presence of $In^{3+}$ that produces crystalline defects, which was because the cubic structure of $InO_2^-$

was not incorporated into the GIZO structure [30]. G.H. Kim et al. [31] reported that as the indium concentration increases, the activation energy for crystallization also increases. When Ga is incorporated into the IZO (GIZO), the transition to the amorphous phase happens in a wider range of In/Zn ratios [32].

Via the ANOVA analysis of the Box-Behnken design, the main positive effect on the crystal size was due to the substrate temperature. This is clearly shown in Fig. 2(a-c). The applied power shows a negative effect, and the films are less crystalline when the power is increased, which is linked to the In/Zn ratio evolution as mentioned and shown in Fig. 3. Fig. 2(d) shows the effect of time on the samples obtained at 80 W and 250º C. These films showed the main peak at 2Ɵ= 31.7º, and two peaks at 2Ɵ= 45.1º and 2Ɵ = 58.8º at a lower intensity corresponding to the (0 0 12), (1 0 8), and (1 0 12) crystallographic planes, respectively (JCPDS 98-016-2451).

Fig. 2(e), shows the comparative XRD patterns for the hexagonal Ga:ZnO (2% Ga), IZO_140_250_30, a GIZO sample, and the cubic $In_2O_3$, all obtained by magnetron sputtering. Fig 2(e-f) shows that the position of the (0 0 n) peaks for the obtained GIZO films changed between from 2Ɵ =34.4º (0 0 2) for the hexagonal 2% Ga:ZnO (ZnO JCPDS 98-016-3383) to 30.3º for the cubic $In_2O_3$ (2 2 2) (JCPDS 98-064-0179).

Comparatively, Fig. 3 presents the position of the c-axis peak (0 0 n) around 31º corresponding to the three GIZO JCPDS standards. 2θ changed from 32.01º corresponding to the $In_2Zn_4O_7$, crystal plane (0 0 12), In/Zn=0.5 (JCPDS 98-016-2451) corresponding to the $In_2Zn_3O_6$, 31.56º plane (0 0 15), In/Zn= 0.66 (JCPDS 98-016-2450), and $In_2Zn_2O_5$, 30.98º (0 0 8), In/Zn=1 (JCPDS 00-020-1442). Fig. 3, also shows 2Ɵ for Ga:ZnO (2% Ga) (In/Zn =0), and the peak (2 2 2) for the cubic $In_2O_3$ (In/Zn =∞), together with the 2Ɵ values for the GIZO samples as function of the In/Zn atomic ratio. Tominaga et al. [32] found a similar evolution when the In/Zn ratio increases. They also reported that the addition of gallium drifts this transition of the 2θ angle to lower values of the In/Zn ratio. This change in the value of the 2θ angle, or planar distance, causes changes in the crystallographic a and c parameters of the hexagonal structure. To discard a potential drift of the position of the 2θ angle of the peak due to a fault of the alignment of the substrate with the goniometer of the XRD device, the planar distances were corroborated by HRTEM, FTT, and SAED. Additional crystalline planes that were not identified by routine XRD were analysed using HRTEM (Fig. 4-5). Fig. 4(a) shows the HRTEM image of a particle obtained by scratching the surface of the GIZO_80_250_60 (In/Zn = 0.55). This film was crystalline as shown by SAED (Fig. 4(b)) and exhibits a hexagonal structure with the crystallographic parameters estimated as a=3.34 Å and c= 33.72 Å close to the values of the JCPDS standard 98-016-2451 (a=3.336 Å and c=33.526 Å, and $In_2O_7Zn_4$). Fig. 4(c-f) shows a zoom image of two areas of this film and the corresponding FFT. Fig. 4(g-h) shows the HRTEM image of a particle of the GIZO_140_150_60 film, with In/Zn =0.99 close to the JCPDS 00-020-1442 (a=3.376 Å, b=23.154 Å, $In_2O_5Zn_2$), and the corresponding SAED (Fig. 4(h)). The SAED in Fig. 4(h) shows a diffuse ring characteristic of a practically amorphous film. The crystal size of this GIZO film was estimated at 2 nm via Scherrer (XRD).

Fig. 5(a-c) shows the EDS and the HRTEM images of the cross-section of the GIZO_140_350_40 (In/Zn = 1.05). The EDS images indicate that the distribution of In (Fig. 5(a)), Zn (Fig. 5(b)) and O (Fig. 6(b)) was uniform through the cross-section of the GIZO film. The selected region in Fig. 5(a) corresponds to the interface glass/GIZO. The film is c-axis textured, with the plane (0 0 8) parallel to the substrate (JCPDS 00-020-1442). The HRTEM images of the cross-section of the GIZO film shown in Fig. 5(d) suggest an initial growth of 3D islands following the Volmer-Weber model, followed by a layer-by-layer growth according the Fran-van de Merwe model. In the first step (Volmer-Weber) the film adatoms are more strongly bound to each other than to the substrate surface, leading to a slow diffusion of the adatoms that formed 3D islands. The islands were not necessarily c-axis oriented, as shown in Fig. 5(d, f), and by the FFT, as presented in Fig. 5(e). In the second step of growth (layer by layer), the crystals were c-axis oriented as shown by the FFT in Fig. 5(g). Nevertheless, crystal grains were connected to each other and no clear grain boundary was observed in the cross-section. The formation of this crystalline morphology, c-axis aligned crystal, was discussed and computer modeled by Shunpei Yamazaki et al. [20].

Fig. 6 shows the FESEM images of the GIZO films obtained at different values of applied power to the target, time, and temperature. In general, the obtained films were very smooth and the roughness decreases with the temperature and with the applied power. By AFM, the GIZO films showed a surface root-mean-square roughness (RMS) of 4 nm for the amorphous GIZO and 11 nm for the crystalline GIZO. The GIZO grains did not exhibit marked sharp edges at the highest power.

### 3. 2 Optical characterisation

When the GIZO films were used as TCOs, and depending on the purpose of the device, the optical behaviour influenced the efficiency of the device, for example, when used as electrodes in solar cells or photocapacitors. From the ANOVA analysis of the Box-Behnken design, the main negative effect on the visible and solar transmittances (Eq. 3-4) was the deposition time. This negative effect of the deposition time on the visible transmittance, as shown in Fig. 7(a), is related to the increase in the thickness, the Beer – Lambert effect. The absorption was proportional to the optical density, product of film thickness t, and the absorption coefficient $\alpha_\lambda$. Fig. 7(a) also shows the solar transmittance, the visible and solar reflectance, and the solar absorptance $\alpha_{solar}$ (Eq. 5). The decay in the transmittance and the increase in the reflectance in the NIR region, as shown in Fig. 8 for four GIZO samples with different thicknesses and carrier densities $n_e$, were linked to the charge carrier density, as will be discussed in Section 3.3. Fig. 8 shows the curve of the sensitivity of the human eye, and the solar AM1.5 spectral irradiance spectrum. Fig. SF2 presents the transmission and reflectance spectra of glass, Ga:ZnO, and GIZO_80_250_60. Fig. 7(b) shows the relationship between the solar absorptance of the GIZO films and the charge carrier density. The solar absorptance for the glass substrate was 8.8 x $10^{-3}$. The solar absorptance increased with the increase in the charge carrier density.

According to Abeles, the relationship between the transmission at a certain wavelength λ, $T_\lambda$, the reflection $R_\lambda$. and the coefficient of absorption $\alpha_\lambda$ is:

$$\alpha_\lambda = \frac{1}{t}\ln\left(\frac{(1-R(\lambda))^2}{T(\lambda)}\right), \tag{6}$$

where t is the film thickness and $\alpha_\lambda$ t is de optical density. The coefficient of absorption $\alpha_\lambda$ was calculated using the Abeles formula and estimated from the extinction coefficient k as obtained from the optical model fitting. The real and imaginary parts of the complex refractive index, n and k, respectively, were obtained via simultaneous fitting of the measured transmittance and reflectance spectra of the films using an optical multilayer stack model GIZO film/glass substrate, susceptibility optical models, and the Fresnel relationships. The total susceptibility χ was obtained by adding various contributions (χi) from several susceptibility models. The frequency-dependent dielectric function of the glass substrate was previously obtained using a sum of Brendel's oscillators and a dielectric background. The GIZO film was optically modelled using a dielectric function model with the O'Leary–Johnson–Lim model [33], an alternative to the Lorentz model [34], to describe the optical spectra in the region of the band gap, and the extended Drude model for the free charge carriers' contribution. The classical Drude (Supplementary Material Eq. SE1) model was used to model the interaction of free charge carriers, such as electrons or holes. This model of the susceptibility has two parameters, the plasma frequency ($\omega_p$), and the damping constant Γ [35, 36], which is inversely proportional to the relaxation time. $\omega_p$ is a characteristic frequency at which the material changes from a metallic to a dielectric response. The plasma frequency $\omega_p$ is proportional to the charge carrier density $n_e$ by

$$\omega_p^2 = \frac{n_e\, e^2}{m^*\, \varepsilon_0}, \tag{7}$$

where e is the electron elementary charge, $\varepsilon_0$ is the permittivity of the free space, and m* the effective mass of the charge carriers that is proportional to $m_e$, the free electron mass, $m^* = n\, m_e$. Although the effective mass of the conduction electrons varies with the carrier concentration, most of the theoretical analyses assume the effective mass is a constant. We estimated the effective mass $m^*$ for the GIZO films at approximately 0.32 $m_e$. This value agrees with the expected values for this kind of conductive n type oxides [37], and is identical to the value obtained by Takagi et al. [38] for single-crystalline GIZO films. The same authors reported 0.34 $m_e$ for amorphous GIZO. Other researchers reported values for m* of approximately 0.2 $m_e$ [39] or 0.3 $m_e$ [34].

The damping constant Γ is related to the charge mobility $\mu_e$ by

$$\mu_e = \frac{e}{m^*\, \Gamma} \tag{8}$$

In the classical Drude model (Eq. SE1), the damping constant does not depend on the frequency ω. In the extended Drude model (Eq. SE2) the damping constant Γ changes smoothly from a constant level at low frequencies $\Gamma_L$ to another constant level at high frequency $\Gamma_H$.

Fig. 9 shows the obtained real and the imaginary parts of the complex dielectric function ($\varepsilon_1$, $\varepsilon_2$), and the complex refractive index (n, k) for Ga:ZnO, and the three GIZO films. Around the plasma frequencies, the contribution due to k became important and $\varepsilon_1$ became negative for frequencies below $\omega_p$, and the free-electron gas had a metallic response with high reflectivity and absorption. For frequencies higher than $\omega_p$, the free electrons could not follow the oscillating electric field, and therefore, the film was transparent at $\varepsilon_1 > o$ and $k < n$. When $\varepsilon_1 < 0$, $k > n$, the reflectance was higher (Fig.8 and Fig. 9b). As $n_e$ increased, the plasma wavelength shifted to shorter wavelengths. The plasma frequencies for the four GIZO films are shown in Fig. 8, from the lower to higher $n_e$, 6621 $cm^{-1}$, 7844 $cm^{-1}$, 8114 $cm^{-1}$, 9837$cm^{-1}$, and the corresponding estimated wavelength for the minima reflectivity $\lambda_{min}$, 1307 nm, 1104 nm, 1067 nm and 880 nm. $\lambda_{min}$ was estimated from [37]:

$$\lambda_p = \lambda_{min}\sqrt{\frac{\varepsilon_\infty}{\varepsilon_{\infty-1}}}, \tag{9}$$

were $\lambda_p$, is the wavelength corresponding to the plasma frequency, and $\varepsilon_{\square}$ is the high-frequency dielectric constant, which was taken as 4. Fig. SF3 shows the spectral absorptance for these four GIZO films.

Tauc's equation expresses the relationship between the absorption coefficient $\alpha_\lambda$ ($cm^{-1}$), the photon energy (hv) (eV), and the energy of the optical band gap $E_g$ (eV):

$$(\alpha_\lambda\, hv) = c\,(hv - Eg)^n\,, \tag{10}$$

where hv is the energy of the incident photon and c is the absorption edge width parameter. The values of Eg can be determined by extrapolating the linear region of the

Tauc plot to hν = 0. The obtained values of the band gap for GIZO were between 3.4 eV obtained for Ga:ZnO and 3.7 eV for pure cubic $In_2O_3$ as shown in Fig. 10.

The optical band gap of the doped TCO films underwent a blueshift by the well-known Burstein-Moss (BM) effect or a redshift caused by the electronic band gap renormalisation [38]. The estimated Burstein-Moss blueshift $\Delta E_{BM}$ may differ also from the experimental data due to the variation in the electron effective mass, which is dependent on the charge carrier density. $\Delta E_{BM}$ can be estimated by the bandgap widening in n-type semiconductor with a parabolic band by the following equation:

$$\Delta E_{BM} = \frac{h^2}{8\,\pi^2 m^*}\,(3\,\pi^2\,n_e)^{\frac{2}{3}}, \tag{11}$$

where, h is Planck's constant. In our case, the band gap shift was estimated as depending on $n_e^{2/3}$. In addition to the Burstein-Moss effect, there may be other subordinate effects or types of imperfections [40]. Moreover, lattice compression can increase the band gap [41]. A clear relationship between the atomic ratio In/Zn or the crystal size with the band gap was not found in the present work. The band gap seemed to grow with the ratio (In/Zn) and the decreasing of crystal size. It has been reported that the band gap of GIZO films with crystalline structure is higher than the band gap of GIZO films with amorphous structure [42]. For amorphous GIZO, there was a decrease in the band gap with the increase in the amount of In [43]. Galca et al. [44] discussed the stoichiometric dependence of the optical properties.

### 3. 3 Electrical properties of GIZO thin films

One of the fundamental relationships describing electrical conduction is

$$\mu_e = \frac{1}{n_e \, e \, \rho_e} \,, \tag{12}$$

where $\mu_e$ is the charge carrier (electron) mobility, and $\rho_e$ (Ω cm) is the electrical resistivity, that is obtained from the sheet resistance $R_{sq}$ (Ω /sq) as $\rho_e = R_{sq}$ t. The electrical conductivity σ is the inverse of the electrical resistivity. From the ANOVA analysis, the applied power to the $In_2O_3$ target was the only factor with a significant effect on the conductivity. This means that there was a linear dependence with the applied power as shown in Fig. SF4. This was because two targets, Ga:ZnO and $In_2O_3$, were used. When other authors used a single mixed target (ZnO:$In_2O_3$) in the same range of applied power, the relationship between the power and conductivity was not linear [45]. However, as shown in Fig. 11(a), the relationship between the conductivity and the In/Zn atomic ratio was not linear. It has been proposed that the increase in the dopant atoms would produce some neutral defects that do not contribute to the conductivity, or ionised impurities and neutral atoms, that can be segregated at the edges of the grains, increasing the scattering of the carriers [46].

Applied power had the largest positive linear effect on the mobility, while the deposition time and substrate temperature had linear negative effects on the electronic mobility with a slight contribution of a positive quadratic effect of the temperature. This means that the increase in the In/Zn ratio increased the mobility, as shown in Fig 11(b). A higher Indium concentration in the GIZO films produced higher mobility, which was confirmed by other reports in the literature [31, 47]. Increasing the temperature and time of deposition decreased the mobility, which was related to the crystalline structure of the film. Increasing the substrate temperature and deposition time increased the crystallinity, as shown in Fig. 2. The effect of the annealing temperature on the mobility was studied by

Makise et al. [48], who found that mobility decreased when the film changed from amorphous to polycrystalline.

The ANOVA analysis found that there were not linear effects on the charge carrier density, and the quadratic effect of the deposition time was the most important factor, as shown in Fig. 12(a). The effects due to the interaction between the power and time and a quadratic effect of the substrate temperature (Fig. SF5), both positive, were less significant. This means that the larger charge carrier density should be obtained at a higher tested time (Fig. 12(a)) and temperature, as shown in Fig. SF5-6. A higher In/Zn ratio should lead to a larger charge carrier density (Fig. 11(a)) and hence higher conductivities, which agrees with Pham et al. [17]. The same trend was obtained by Kumar et al. [39] for undoped amorphous IZO. The charge carrier density found by these authors ranges from 1.26 x$10^{20}$ cm$^{3}$ (In/Zn = 0.52) to 3.73 x $10^{20}$ cm$^{3}$ (In/Zn =0.86). These are similar to those found in this work, where the charge carrier density obtained ranges from 1.56 x $10^{20}$ (In/Zn =0.68) to 3.45 x $10^{20}$ cm$^{3}$ (In/Zn = 1.15), as demonstrated in Table ST3. However, as shown in Fig. 12(b), the charge carrier density increased for each applied power with the In/Zn ratio, but this evolution segregated into three groups. This separation into three groups could be related to the crystallographic structure undergoing a decrease in the charge carrier density due to changes in the crystalline parameters of the hexagonal structure with further increases in the In/Zn ratio, as noted in Section 3.1. The maximum values for each group in Fig. 12(b) were achieved for the optimal combination of temperature and time, as shown in Fig. SF6. Takeda et al. [49] reported an increase in mobility when the charge carrier density increased.

For the optimisation of TCOs, a compromise between conductivity and transparency is necessary, and for this purpose, different figures of merit (FOM) have been defined.

Fraser and Cook [50] proposed using the ratio of transmission at a given wavelength and sheet resistance to characterise the TCO films. Haacke [22] suggested the figure of merit

$$\Phi_{TC} = T_{550}^{10} / R_{sq} = \sigma \, t \exp(-10 \, \alpha_{\lambda} \, t), \tag{13}$$

where $R_{sq}$ is the sheet resistance and T is the optical transmission (scale 0-1) at 550 nm. This merit function uses the exponent 10 with the intention of reducing the excessive weight of the sheet resistance in $\Phi_{TC}$. Gordon [23] suggested using the conductivity/absorption coefficient ratio $\sigma/\alpha_{\lambda}$. Fernández et al. [51] proposed

$$\Phi_F = -1/\rho \ln(T) = \sigma \quad \alpha_{\lambda} \quad t \tag{14}$$

There are other proposals [52]. More recently, Hu et al. [24] proposed a modified form of the Haacke equation

$$\Phi_H = \frac{\left(\frac{Q_A}{Q_T}\right)^{10}}{R_{sq}}, \tag{15}$$

where $Q_A$ and $Q_T$ are the numerator and denominator of Eq. 4, respectively. Therefore, $Q_A/Q_T$ is the solar transmittance $T_{solar}$, corrected by a specific external quantum function for each kind of solar cells in which the TCO is used and limiting the range of wavelength to the absorbable waveband of the specific solar cell. However, Hu et al. [24] did not define the figure of merit $\Phi_H$ for the visible region. Transparency in the visible range is important for several applications in transparent electronics or smart windows. We propose replacing the solar spectra irradiance AM1.5 with the theoretical illuminant $D_{65}(\lambda)$ as proposed by CIE [25] and the specific external quantum function by $V(\lambda)$ for the visible region. Here, $V(\lambda)$ plays the same role as the external quantum function, and the ratio $Q_A/Q_T$ of Eq. 15 converts in the visible transmittance $T_{vis}$, resulting in the modified forms of $\Phi_{TC}$.

$\Phi_{TCMvis} = T_{vis}{}^{10}/R_{sq}$ (16)

and

$\Phi_{Hsolar} = T_{solar}{}^{10}/R_{sq}$, (17)

where $\Phi_{Hsolar}$ is $\Phi_H$ without the specific external quantum function. Both FOMs are shown in Fig. 13(a).

In the same way, we have also modified the FOMs proposed by Fernández et al. (Eq.14)

$\Phi_{FMvis} = -1/\rho \ln (T_{vis})$ (18)

$\Phi_{FMsolar} = -1/\rho \ln (T_{solar})$ (19)

and the Gordon's FOM, $\alpha_{solar}$ as calculated by Eq. 5,

$\Phi_{GMsolar} = \sigma/\alpha_{solar}$ (20)

These FOMs are represented in Fig. 13(c-d). We have also defined two new FOMs for the visible region and solar region

$\Phi_{Mvis} = T_{vis}/\rho$ (21)

$\Phi_{Msolar} = T_{solar}/\rho$, (22)

where ρ is the electrical resistivity (Ω cm). We consider resistivity more suitable that sheet resistance because ρ considers the film thickness t, $\rho = R_{sq}$ t. Both FOMs have similar behaviour, as shown in Fig. 13(b).

All of the FOMs were fitted by a second-degree polynomial. In our case, we were interested in selecting the optimum In/Zn atomic ratio based on the best balance between the conductivity and transparency. For our GIZO films, $\Phi_{Hsolar}$ behaved well to find the In/Zn ratio that provided the best balance for the solar region (Fig. 13(a)), but $\Phi_{TCMvis}$ did not. $\Phi_{Hsolar}$ shows a maximum for In/Zn= 0.89, while $\Phi_{TCMvis}$ increased. The opposite behavior occurred with $\Phi_{FMvis}$ and $\Phi_{FMsolar}$, as shown in Fig. 13(d). Fig. 13(c) demonstrates $\Phi_{GMsolar}$ with a maximum for In/Zn=0.86. $\Phi_{Mvis}$ and $\Phi_{Msolar}$ show maximums around In/Zn= 0.95 and In/Zn = 0.93, respectively. $\Phi_{Mvis}$ and $\Phi_{Msolar}$ indicate a similar evolution with the In/Zn ratio in contrast to the other FOMs (Fig. 13).

The best values of electrical conductivity were obtained for the GIZO films with In/Zn ratio ≥ 1, the best reached value of conductivity 1.75 x $10^3$ $\Omega^{-1}$ $cm^{-1}$, and improving the conductivity of pure ZnO, gallium zinc oxide (GZO) [53] and for other GIZO films deposited using the sputtering method [54, 55], the visible and solar transmittances were below 0.8. It is accepted that visible transmittance should not be below 80% for a TCO. Despite these individual maximum values of conductivity, it should be expected that the best balance of conductivity and transparency will be obtained for the In/Zn ratio corresponding to the maximum values of the FOMs, therefore, the GIZO films with the nearest ratios to the maximum values of the FOMs, approximately 0.9. In/Zn 0.83, 0.85 have conductivities of 1102, 1300 $\Omega^{-1}cm^{-1}$, visible transmittances of 81%, 83%, and solar transmittances of 73%, 75% respectively (glass/GIZO films). The measured transmittances of the glass substrate were 92.5% and 92.2% for $T_{vis}$ and $T_{solar}$, respectively. The losses of 7.5% and 7.8% in the visible and solar light transmission were due to reflection by the glass substrate. Thus, the In/Zn ratios between 0.85-0.90 were optimal for the GIZO films (2% Ga/Zn) as TCOs for visible and solar applications.

## 3. Conclusions

Conductive and transparent GIZO films were successfully deposited on glass substrates with a fixed Ga /Zn ratio of 0.02. Using a Box-Behnken experimental design approach, the effects of the magnetron sputtering parameters were determined, namely, the power applied to the $In_2O_3$ target, substrate temperature, and deposition time, on the structural, optical, and electrical properties of the GIZO films. The thickness increased linearly with the deposition time and the power applied to the $In_2O_3$ target, and the In/Zn ratio also increases with the applied power. The crystalline parameters of the hexagonal structure changed with the In/Zn ratio and the charge carrier density was linked to those changes and therefore to the GIZO stoichiometry. The GIZO films grew c-axis oriented after an initial island step. The small percentage of Ga introduced early amorphisation that led to an increase in the carrier mobility and conductivity. The increase in the solar absorptance due to the increase in the spectral absorptance in the NIR region was related to the plasma frequency and therefore to the charge carrier density. New FOMs were proposed that use integrated values, weighted by functions for visible and solar, instead of the individual of the average values for the transmitted radiation or the absorption coefficient. The defined figures of merit indicated that the best balance between conductivity and transparency for visible and solar applications of the GIZO films (2% Ga/Zn) as TCOs were in the In/Zn of 0.85-0.90 range.

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**Figure captions.**

**Fig. 1**. (a) In/Zn atomic ratio versus power applied to the $In_2O_3$ target (b) Thickness versus deposition time.

**Fig. 2**. XRD patterns of samples obtained at (a) 80 W (b) 110 W (c) 140 W and different temperatures. (d) XRD spectra of the samples obtained at 80W, 250ºC and different times. (e) XRD spectra of the Ga:ZnO, $In_2O_3$ and a GIZO sample. (f) Normalized XRD spectra of (1) Ga:ZnO, (2-4) GIZO at 40 min, 350ºC and 80, 110, 140 W respectively; (5) $In_2O_3$

**Fig. 3.** 2θ position of the plane (0 0 n) versus the In/Zn atomic ratio: (filled circles) JCPDS standards corresponding to ZnO, $In_2Zn_4O_7$, $In_2Zn_3O_6$, $In_2Zn_2O_5$ and $In_2O_3$; (open circles) GIZO samples. Crystal size versus the In/Zn atomic ratio (triangles).

**Fig. 4.** HRTEM image (a) of a particle of GIZO_80_250_60 (b) SAED, (c, f) Zoom of partial areas of the particle, (e, f) FFT of the zoomed areas. (d, e). HRTEM image of the particle of GIZO_140_150_40 (g) and the corresponding SAED (h).

**Fig. 5**. (a-c) EDS images of the cross section of the GIZO_140_40_350; (d) HRTEM image of the cross section; (e, f) HRTEM images of the zoomed areas of the cross section (g, h) FFT of the zoomed areas.

**Fig. 6.** FE-SEM micrographs surface images of the samples obtained at (a) GIZO_80_250_60 (b) GIZO_110_150_60 (c) GIZO_140_150_40 (d) GIZO_140_350_40.

**Fig. 7.** (a) Visible and solar transmittance and reflectance, and solar absorptance, versus film thickness (b) Solar absorptance versus charge carrier density

**Fig. 8.** (a) Curve of sensitivity of the human eye, (b) AM1.5 spectral irradiance. Transmittance and reflectance spectra for GIZO films: (c) GIZO_110_150_20, In/Zn= 0.68, t=175 nm, $n_e = 1.56 \times 10^{20}$ cm$^{-3}$; (d) GIZO_140_250_20, In/Zn=1.01, t= 202 nm, $n_e = 2.19 \times 10^{20}$ cm$^{-3}$; (e) GIZO_110_150_60, In/Zn=0.97, t= 488 nm, $n_e = 2.35 \times 10^{20}$ cm$^{-3}$; (f) GIZO_140_250_60; In/Zn= 1.15, t= 536 nm, $n_e = 3.45 \times 10^{20}$ cm$^{-3}$.

**Fig. 9.** Real and imaginary parts of the complex refractive index (a) and the dielectric constant (b) for the samples: (1) Ga:ZnO (2% Ga), (2) GIZO_110_150_20, (3) GIZO_140_250_20 , (4) GIZO_140_250_60.

**Fig. 10**. Tauc's plos for films (1) Ga:ZnO (2% Ga) and GIZO (2) GIZO_110_150_20, (3) GIZO 110_150_60, (4) GIZO_140_350_40, (5) GIZO_110_350_60.

**Fig. 11.** (a) Conductivity and (b) carrier mobility versus In/Zn atomic ratio

**Fig. 12**. Charge carrier density versus (a) deposition time (b) In/Zn atomic ratio

**Fig. 13**. FOMs versus In/Zn atomic ratio: (a) $\Phi_{Hsolar}$ (triangles), $\Phi_{TCMvis}$ (circles) (b) $\Phi_{Msolar}$ (triangles), $\Phi_{Mvis}$ (circles) (c) $\Phi_{GMsolar}$ (d) $\Phi_{FMvis}$ (circles), $\Phi_{FMsolar}$ (triangles)