Available online at www.sciencedirect.com

ScienceDirect

Energy Procedia 84 (2015) 183 – 189

Energy Procedia

E-MRS Spring Meeting 2015 Symposium C - Advanced inorganic materials and structures for photovoltaics

Relation between sputtering parameters and optical and electrical properties of Ga doped ITO transparent conductive oxide

Marko Berginc[a], Andrej Čampa[a], Katarina Vojisavljević[b], Barbara Malič[b], Peter Panjan[b], Marko Topič[a]

[a]*University of Ljubljana, Faculty of Electrical Engineering, Laboratory of Photovoltaics and Optoelectronics, Tržaška cesta 25, 1000 Ljubljana, Slovenia*

[b]*Jožef Stefan Institute, Jamova cesta 39, 1000 Ljubljana, Slovenia*

Abstract

A ceramic target with Ga:In:Sn=4:64:32 metal ratio has been sintered and used for RF sputtering process to develop high quality Ga doped ITO (GITO) transparent conductive oxide layers, particularly for photovoltaic applications. The sputtering parameters (sputtering power, oxygen flow, and substrate temperature) have been varied first and optimized with respect to the resistivity measurements. The layers deposited under optimized conditions were then post-annealed at different temperatures (200 – 500 ºC) either in the air or in nitrogen atmosphere in order to further improve the conductivity. The deposited 200 nm thick GITO layer has high electron mobility (50 cm^2/Vs) at relatively low resistivity (0.90 mΩcm) although the free electron concentration is kept low (1.4×10^{20} cm^{-3}) to prevent excessive free-carrier absorption. Thus, high transmission of the layer (~80% at 400 – 1500 nm) is obtained.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Peer-review under responsibility of The European Materials Research Society (E-MRS)

Keywords: Transparent conductive oxide; Ga doped ITO; RF sputtering; post-annealing

1. Introduction

Transparent conductive oxides (TCOs) are utilized in a broad selection of applications such as gas sensors, displays, light emitting diodes, for airplane windows heating, low emission glass, *etc*. As a contact they are irreplaceable for different thin-film photovoltaic technologies. In additions to a low sheet resistance (5 – 10 Ω/□) and high optical transparency over a broad wavelength range (>80% at 400 – 1000 nm), low TCO to metal contact resistance, appropriate (either low or high) light scattering, high temperature stability and stability under hydrogen exposure in plasmas, are usually required. Nowadays a variety of different TCOs exist [1-12] containing different

1876-6102 © 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Peer-review under responsibility of The European Materials Research Society (E-MRS)
doi:10.1016/j.egypro.2015.12.312

metal oxides (like SnO_2:F - FTO, SnO_2:In - ITO, ZnO:Al - AZO, *etc.*) and with various metal ratios. The most commonly used TCO is SnO_2:In (ITO) particularly with In:Sn = 90:10 metal ratio since it has a low optical absorption but still very good electrical conductivity. However, its main disadvantage is relatively high cost due to high indium content. Therefore, much research effort was undertaken to completely eliminate or at least reduce the indium consumption but at the same time maintain advanced optical and electrical properties. One potential candidate is Ga doped ITO (GITO) with Ga:In:Sn=4:64:32 metal ratio which is the subject of presented study.

A ceramic target and RF sputtering have been used to deposit high quality GITO layers. The sputtering parameters (sputtering power, oxygen flow, and substrate temperature T_s) have been varied in order to determine optimal sputtering conditions regarding the electrical properties of the layers. The layers deposited under optimized sputtering conditions have been post-annealed at different temperatures (T_a) in air or in N_2 atmosphere and the influence of T_a on the electrical properties is presented. Finally the optical and electrical properties of the best layer are given.

2. Experimental

2.1. Target preparation

Within the ternary system Ga_2O_3-In_2O_3-SnO_2 a composition with Ga:In:Sn=4:64:32 metal ratio was proposed as the composition that can meet the criteria for obtaining high quality films with required functional properties.

The following oxide reagents were used for the target processing: Ga_2O_3 (99.999%, cat. no. 10508, Alfa Aesar Puratronic, Karlsruhe, Germany), In_2O_3 (99.997%, cat. no. 10709, Alfa Aesar Puratronic, Karlsruhe, Germany) and SnO_2 (99.9%, cat. no. 12283, Alfa Aesar Puratronic, Karlsruhe, Germany).

Prior the powder mixture processing, the Ga_2O_3 and In_2O_3 powders were preliminary milled in a planetary mill (Retsch PM400, Retsch GmbH, Haan, Germany, zirconia vials and balls) for 8 h and 4 h, respectively, in isopropyl alcohol (IPA) in order to break up the agglomerates and ensure the particle size distribution similar to the one observed in SnO_2 (d_{50}=0.324 μm). Thereafter, the powders were mixed in a stoichiometric Ga:In:Sn=4:64:32 metal ratio, homogenized in a planetary mill in IPA for 2 h and dried at 90 ºC. In addition, the powder mixture was subjected to a high energy milling process of mechanical activation over a period of 48 h.

The powder mixture was pressed into pellets of 68 mm in diameter at 50 MPa and subsequently by cold isostatic pressing at 300 MPa. The pellet was sintered in air to 1400 ºC, followed by 10 h dwell time, and heating/cooling rates of 2 ºC/min. The coexistence of a T-phase of $Ga_{3-x}In_{5+x}Sn_2O_{16}$ along with Sn- or/and Ga- substituted In_2O_3 bixbyite phase confirmed by X-ray analysis, is in agreement with the phase diagram for the ternary Ga_2O_3-In_2O_3-SnO_2 system at 1250 ºC. The phase transformation of existing phases or the formation of new phases should be expected only above 1400 ºC [13,14]. The sintered GITO target with 55 mm in diameter and density of 5.78 g/cm^3 was plan-parallel fine-ground, etched to remove any impurities introduced in the process of fine-grinding, annealed at 600 ºC in oxygen and used for RF sputtering of thin films.

2.2. Sputtering

A Sputron sputtering system (Oerlikon Balzers) was used for GITO layer deposition. It uses low voltage thermionic arc as a source of ions for sputtering. A plasma beam (typically 40 V/40 A) is produced between the hot filament (Ta wire) and the auxiliary anode around the target. Arrangements of this type are usually referred as triode or tetrode sputtering system. The target-substrate distance is about 225 mm. Substrates (Corning Eagle glass, 1 mm thick) were mounted on a planetary drive system which permits a double rotation of substrates, therefore the deposition rate and thickness reproducibility were better than 2%. The substrates were out of plasma, thus it is possible to keep the T_s below 100 °C. When needed, we use quartz lamps for substrates heating up to 180 ºC. The common deposition parameters used in this study were: background pressure below 5×10^{-7} mbar, argon pressure 2×10^{-3} mbar, and the target current 0.6 A. Other deposition parameters have been varied and are given and described in Results and Discussion section.

2.3. Structural, optical and electrical characterization

The X-ray photoelectron spectroscopy (XPS) analyses were carried out on spectrometer (PHI-TFA XPS, Physical Electronics Inc.) in ultra-high vacuum (8×10^{-10} mbar). Sample surfaces were excited by X-ray radiation from monochromatic Al source (photon energy 1486.6 eV). The analyzed area was 0.4 mm in diameter and the analyzed depth was about 3 – 5 nm. Quantification of surface composition was performed from XPS peak intensities taking into account relative sensitivity factors provided by the instrument manufacturer [15]. Sensitivity of the XPS is about 0.2 at.%. Depth distribution analysis of elements was performed with the XPS in combination with ion sputtering (Ar ions, energy 3 keV).

The UV-VIS optical measurements (total transmission – T_{tot} and reflection – R_{tot}) were scanned using a Lambda 950 Perkin Elmer spectrophotometer. The layers on glass substrates were scanned from 1500 to 300 nm in decrements of 10 nm, while light was collected using a 150 mm Ulbricht integration sphere coated with Spectralon. Absorption was calculated afterwards as $A=1-R_{tot}-T_{tot}$. The thickness of the GITO layers (d) was determined from two specular transmittance spectra measured at known polarization and at two different incident angles. The Nika software tool was then used for accurate calculation of the d, which is determined in addition to the wavelength dependent extinction coefficient (k) and refractive index (n) [16].

For electrical characterization we measured sheet resistance R_{sh} first using a RIG Mode C (A.&M. Fell) 4-probe head and a Keithley 2602 source meter. Then the resistivity (ρ) was calculated using the known R_{sh} and d. The Hall mobility of the electrons μ_e was measured with calibrated in-house Hall set-up consisting homogenous permanent magnetic field in the area of measurements (B=0.634 T). A Keithley 2602 source meter was used for current injection and a HP3457A multimeter to measure the Hall voltage. Finally a concentration of free electrons (n_e) was calculated from ρ and μ_e.

3. Results and discussion

Herein we study the development of the GITO layers. First we studied how different sputtering parameters (sputtering power, oxygen flow, and T_s) influence the ρ of the layers. Then we used optimized sputtering parameters to deposit a batch of GITO layers which were post-annealed at different T_a either in air or in N_2 atmosphere. The best layer obtained was optically (T_{tot}, R_{tot}, A, d) and electrically (R_{sh}, ρ, μ_e, n_e) characterized.

The sputtering parameters that have been varied and resulting ρ of the layers before annealing (as deposited) and after annealing (annealed) are gathered in Table 1. The GITO target has relatively low resistance therefore a DC sputtering mode was chosen first while the sputtering power was gradually increased to 1000W (batch #1). The layers had a relatively low resistivity (2.59 Ωcm) but they were opaque. Moreover the target cracked during the deposition. Since the deposition rate was not crucial for our study we used less stressful sputtering conditions for the following batches, *i.e.* an RF sputtering mode with reduced power (750 W).

Table 1. The influence of sputtering parameters on ρ of the GITO layers before annealing (as deposited) and after 30 min post-annealing at optimal T_a.

Batch #	Sputtering (DC/RF)	Power (W)	O_2 flow (cm^3/min)	T_s (ºC)	Deposition rate (nm/min)	ρ as deposited (Ωcm)	T_a (ºC)	ρ annealed (mΩcm)
1	DC	1000	0.0	65	7.5	2.59±0.15 Ωcm	420 ºC in air	8.67±0.17
2	RF	750	4.1	80	3.3	86.6±11.1 kΩcm	420 ºC in air	5.08±0.67
3	RF	750	7.0	80	3.7	0.63±0.06 Ωcm	500 ºC in air	5.68±0.80
4	RF	750	7.0	160	5.2	0.70±0.10 Ωcm	250 ºC in air	4.01±0.16
5	RF	750	0.0	170	4.3	1.17±0.08 mΩcm	200 ºC in air	1.13±0.05
						1.46±0.16 mΩcm	340 ºC in N_2	0.90±0.05
6	RF	750	1.8	170	4.2	4.43±0.10 mΩcm	500 ºC in N_2	0.97±0.05

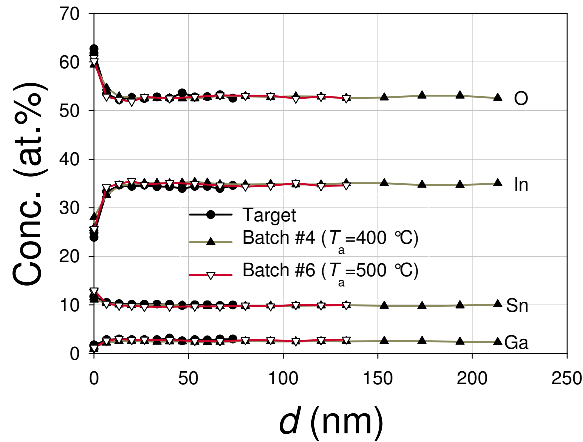

Fig. 1. The XPS depth profile of Ga, In, Sn and O in the target and GITO layers (batch #4 annealed at 400 ºC and batch #6 annealed at 500 ºC).

A 4.1 cm^3/min O_2 flow was used for the batch #2. No additional cooling or heating of the substrate was applied and the substrates were let to self-heat to T_s=80 ºC. The ρ was immense (*i.e.* 86.6 kΩcm) therefore the oxygen flow was increased to 7.0 cm^3/min in batch #3 in order to increase the n_e. Although ρ significantly decreased (0.63 Ωcm) it remained too high for optoelectronic applications. Similar ρ (*i.e.* 0.70 Ωcm) was obtained in batch #4 where the substrates were heated to T_s=160 ºC during the deposition. On the other hand the oxygen flow was set to zero for batch #5 and the substrates were heated to T_s=170 ºC again. In this case a significant reduction of ρ was observed (*i.e.* 1.17 – 1.46 mΩcm) but then it increased to 4.43 mΩcm when oxygen flow increased to 1.8 cm^3/min (batch #6).

All layers presented above have been post-annealed in air and/or in N_2 atmosphere at different post-annealing temperature T_a. Usually conductivity improved for several decades (Table 1) whereas the optimal T_a strongly depends on sputtering parameters; the higher the substrate temperature during the deposition (T_s) the lower is the optimal T_a. Furthermore, conductivity improvement also strongly depends on the atmosphere where the post-annealing was performed (either in air or in N_2 atmosphere).

The sputtering parameters and post-annealing treatment are expected to influence the chemical composition of the samples particularly the Ga and O concentration therefore we performed the XPS analysis of the target and two different samples (*i.e.* batch #4 annealed at 400 ºC and batch #6 annealed at 500 ºC). The XPS results show very good agreement between the target composition and composition of the layers although significantly lower O_2 flow was used in batch #6 compared to batch #4 (1.8 *vs.* 7.0 cm^3/min) and slightly higher T_a (500 *vs.* 400 ºC). Furthermore, the target and the layers showed similar and uniform depth composition (15 – 130 nm). However, we observed that the composition on the surface (0 – 15 nm) of the layers differs slightly from the composition in the bulk; on the surface there is a small enrichment of Sn and O and a small depletion of In and Ga with respect to composition in the bulk. The reason for this is (i) preferred formation of SnO_2 at the surface and/or (ii) preferential sputtering of some elements due to Ar-ion bombardment which results in slightly modified composition. Nevertheless, the compositions of analyzed layers are very similar to target's composition.

The effect of different T_a in the air and in the N_2 atmosphere on the ρ of batch #5 layers is presented in Fig. 2a and b. The ρ does not change significantly after post-annealing in the air at 200 – 250 ºC but it increases for 25% after annealing at 300 ºC (Fig. 2a). On the contrary, post-annealing in N_2 atmosphere in 200 ºC<T_a<500 ºC range always reduce the ρ (Fig. 2b). The relative improvement of the layer's conductivity gradually increases with increasing T_a in 200 – 340 ºC range. At T_a=340 ºC the best conductivity improvement was observed, *i.e.* the ρ decreases for 38% after post-annealing. Additionally, higher T_a also improves the conductivity but a relative decrease in ρ is saturated at around 22-24%.

The results are in agreement with Hu *et al.* who also found an increase in ρ when ITO layers were post-annealed

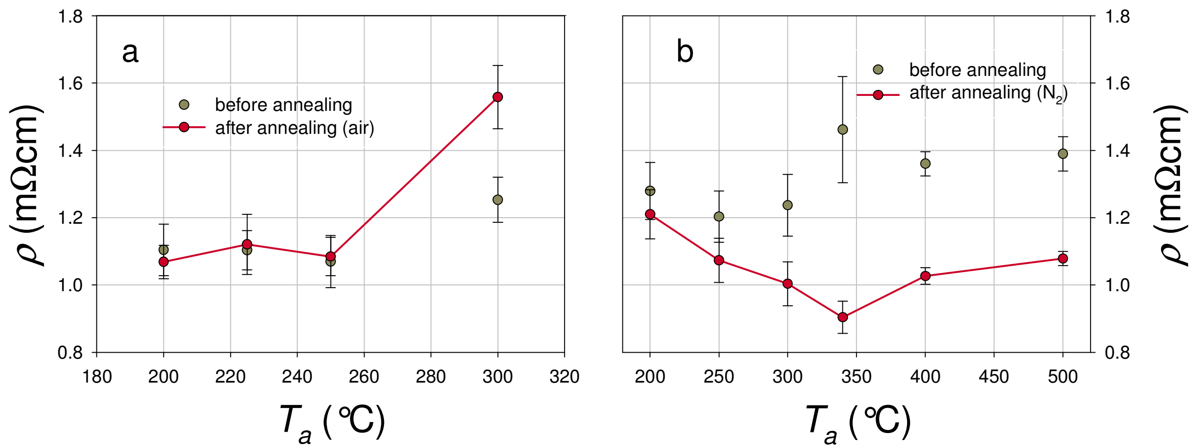

Fig. 2. The influence of T_a on the ρ of the GITO layers that were post-annealed in air (a) or in N_2 atmosphere (b).

in the air while ρ decreased after post-annealing in the vacuum [17]. This is due to the reaction between ITO layer and O_2 in the air, which decreases the oxygen vacancies and the carrier concentration and in turn increases ρ [17]. On the other hand, post-annealing in vacuum improves the crystallinity of the layers [17,18] and even allow some oxygen atoms that are adsorbed at surface of the layer to escape and consequently increase the n_e and decrease the ρ [17]. Furthermore, Lee *et al.* [18] showed that 0.1 wt.% Ga doped ITO layer remains amorphous up to T_a=220 °C in vacuum while it remains amorphous up to T_a=250 °C when doping with Ga was increased to 2.9 wt.%. This indicates that the ITO:Ga layers crystallize at higher temperatures than the ITO layers and that the amorphisation of ITO layers increases with increasing Ga content [18].

The optimal sputtering conditions determined so far are: RF sputtering mode, sputtering power 750 W, no additional oxygen during deposition, high substrate temperature (T_s=170 °C) during the deposition and post-annealing at T_a=340 °C in N_2 atmosphere. The optical properties (T_{tot}, R_{tot}, A) of the best 200 nm thick GITO layer on a glass substrate (batch #5) are shown Fig. 3. It has relatively high T_{tot} (~80% at 400 – 1500 nm) and very low A; the extinction coefficient (k) of the GITO layer is even smaller than k of state-of-the-art ITO layers (not shown here). Low absorption losses are related to low free-carrier absorption, *i.e.* low n_e (Table 2). Despite low n_e a relatively good ρ (0.90 mΩcm) was obtained due to good μ_e (50 cm^2/Vs), Table 2.

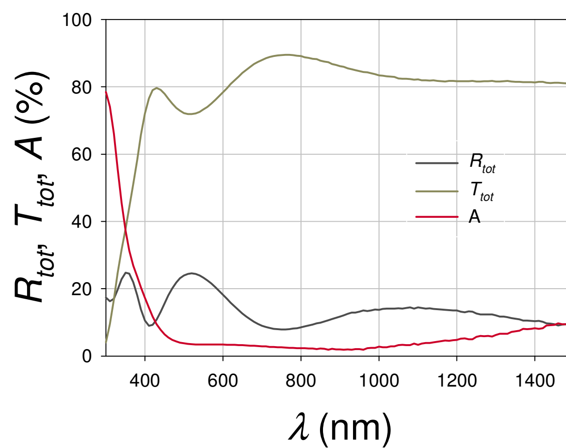

Fig. 3. The T_{tot}, R_{tot} and A of the GITO layer (d=200 nm) deposited under optimized sputtering conditions and post-annealed at T_a=340 °C in N_2.

Table 2. Electrical properties of the GITO layer deposited under optimized sputtering conditions and post-annealed at T_a=340 ºC in N_2.

Electrical parameter	Value
Thickness d	200 nm
Sheet resistance R_{sh}	45.2 Ω/□
Resistivity ρ	0.90 mΩcm
Electron mobility μ_e	50 cm^2/Vs
Electron concentration n_e	1.4×10^{20} cm^{-3}

Further improvements in ρ might be obtained by increasing the T_s and/or by increasing the sputtering time at lower sputtering power as suggested by Choi *et al.* [19]. Additionally, small oxygen flow (<1.8 cm^3/min) might increase the n_e and reduce ρ.

4. Conclusions

The ceramic target with Ga:In:Sn=4:64:32 metal ratio and an RF sputtering under different sputtering conditions have been used to deposit Ga doped ITO (GITO) transparent conductive oxides. The optimal layer regarding the conductivity was obtained when sputtering at 750 W without additional oxygen and at 170 ºC substrate temperature was used. These optimized layers were then post-annealed at different temperatures in the air or in the N_2 atmosphere. Post-annealing in the air did not improve the conductivity whereas it was improved for 38% after annealing at 340 ºC in N_2 atmosphere. The final GITO layer has resistivity 0.90 mΩcm, free electron mobility and concentration 50 cm^2/Vs and 1.4×10^{20} cm^{-3}, respectively. At the same time good optical properties (transmission ~80% at 400 – 1500 nm) due to low free carrier absorption is obtained.

Acknowledgements

Slovenian Research Agency (contract number J2-5466) is acknowledged for funding this study. The work was also partially funded by the Slovenian Research Agency under the P2-0197 program.

References

[1] Fortunato E, Barquinha P, Martins R. Oxide Semiconductor Thin-Film Transistors: A Review of Recent Advances. Advanced materials 2012; 24: 2945-2986.
[2] Liu HY, Avrutin V, Izyumskaya N, Ozgur U, Morkoc H. Transparent conducting oxides for electrode applications in light emitting and absorbing devices. Superlattices And Microstructures 2010; 48: 458-484.
[3] Hoel CA, Mason TO, Gaillard JF, Poeppelmeier KR. Transparent Conducting Oxides in the ZnO-In_2O_3-SnO_2 System. Chemistry Of Materials 2010; 22: 3569-3579.
[4] Beyer W, Hupkes J, Stiebig H. Transparent conducting oxide films for thin film silicon photovoltaics. Thin Solid Films 2007; 516: 147-154.
[5] Exarhos GJ, Zhou XD, Discovery-based design of transparent conducting oxide films. Thin Solid Films 2007; 515: 7025-7052.
[6] Hosono H. Recent progress in transparent oxide semiconductors: Materials and device application. Thin Solid Films 2007; 515: 6000-6014.
[7] Fortunato E, Ginley D, Hosono H, Paine DC. Transparent conducting oxides for photovoltaics. MRS Bulletin 2007; 32: 242-247.
[8] Cao E, Li J, Chen H, Xue J. Transparent electrodes for organic optoelectronic devices: a review. Journal of Photonics for Energy 2014; 4: 040990.
[9] Calnar S, Tiwari AN. High mobility transparent conducting oxides for thin film solar cells. Thin Solid Films 2010; 518: 1839-1849.
[10] Granqvist CG. Transparent conductors as solar energy materials: A panoramic review. Solar Energy Materials and Solar Cells 2007; 91: 1529-1598.
[11] Ohta H, Hosono H. Transparent oxide optoelectronics. Materials Today 2004; 7: 42-51.
[12] Granqvist CG, Hultåker A. Transparent and conducting ITO films: new developments and applications. Thin Solid Films 2002; 411: 1-5.
[13] Edwards DD, Mason TO. A new transparent conducting oxide in the Ga_2O_3–In_2O_3–SnO_2 system. Applied Physics Letters 1997; 70: 1706-1708.
[14] Edwards DD, Mason TO. Phase equilibria in the Ga_2O_3–In_2O_3 system. Journal of the American Ceramic Society 1997; 80: 253-257.
[15] Moulder J.F., Stickle W.F., Sobol P.E., Bomben K.D. Handbook of X-Ray Photoelectron Spectroscopy. Minnesota: USA; 1995.

[16] Čampa A, Krč J, Smole F, Topič M. Determination of optical constants of thin amorphous silicon films by reflectance and transmittance measurements. 41th International Conference on Microelectronics, Devices and Materials and the Workshop on Green electronics, 14.-16. September 2005, Ribno, Slovenia.
[17] Hu Y, Diao X, Wang C, Hao W, Wang T. Effects of heat treatment on properties of ITO films prepared by rf magnetron sputtering. Vacuum 2004; 75: 183-188.
[18] Lee HJ, Song PK. Crystallinity, etchability, electrical and mechanical properties of Ga doped amorphous indium tin oxide thin films deposited by direct current magnetron sputtering. Thin Solid Films 2014; 559: 53-57.
[19] Choi JH, Kang SH, Oh HS, Yu TH, Sohn IS. Design and characterization of Ga-doped indium tin oxide films for pixel electrode in liquid crystal display. Thin Solid Films 2013; 527: 141-146.