THE PUBLISHING HOUSE
OF THE ROMANIAN ACADEMY

PROCEEDINGS OF THE ROMANIAN ACADEMY, Series A,
Volume 15, Number 2/2014, pp. 146–150

ON THE ELECTRICAL PROPERTIES OF TRANSPARENT ELECTRODES

Mihaela GIRTAN[1], Romain MALLET[2]

[1] Angers University, Photonics Laboratory, Angers, France
[2] Angers University, SCIAM, LUNAM, Angers, France
Corresponding author: Mihaela GIRTAN, E-mail: `Mihaela.Girtan@univ-angers.fr`

In this paper we present the electrical properties of the typical transparent electrodes (ITO, AZO, IZO, FTO, PEDOT:PSS, etc.) prepared by different methods such as: spray pyrolysis, sputtering, sol-gel, thermal oxidation, PLD, etc. The modifications of electrical properties of electrodes during the sun exposure of the devices may explain some of problems arising in the I-V characterization of third-generation solar cells. The electrical resistivity stability of transparent electrode thin films as a function of the temperature is analysed in detail.

Keywords: transparent electrodes, third-generation solar cells.

1. INTRODUCTION

Solar cells based on Silicon bulk or GaAs bulk p-n junctions are considered as the “first generation” solar cells. Amorphous silicon, CIS, CIGS, and CdTe thin films solar cells correspond to the “second generation”. Organic and hybrid thin films solar cells represent the “third generation”. The classical architecture of “third generation” cells is described in Fig.1. In the case of organic solar cells, the active layer is a mixture of organic materials, in most of cases of PCBM fullerene derivative and the P3HT conducting polymer [1–5]. For hybrid solar cells, the active material is a mixture of organic and inorganic materials (dyes, TiO_2, iodine electrolytes) [6]. Different from the first generation, the second and third generation solar cells architecture involves the presence of thin films transparent electrodes. The common transparent electrodes for these cells are ITO (Tin-doped Indium Oxide) thin films and FTO (Fluorine-doped Tin Oxide) thin films.

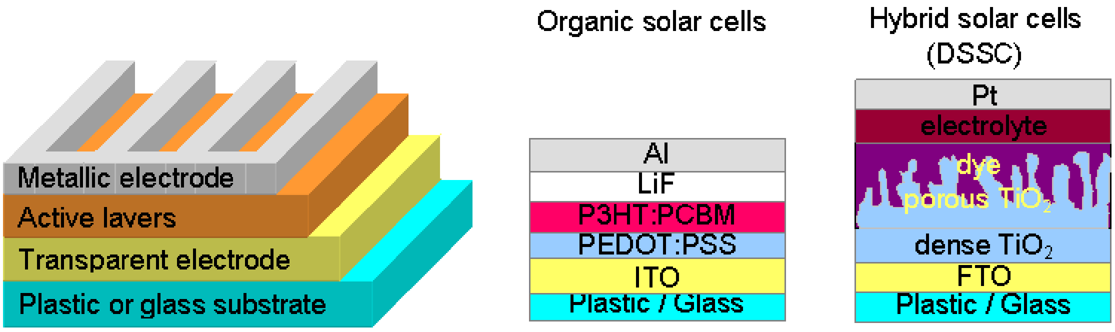

Fig. 1 – Third generation solar cells architecture.

Besides the electrical conductivity and optical transparency, the most important characteristics of these electrodes, especially in the case of the third generation solar cells, are the following: the stability of the electrical properties, their roughness, and work function. ITO is the common transparent electrode used in the third generation solar cells. However, the relative high cost and scarceness of indium conduct to the necessity to find alternative solutions in order to replace ITO with other transparent electrodes or to reduce the quantity of the material in the transparent films, by keeping at the same time, the optimal characteristics in terms of electrical conductivity, work function, and surface roughness. This paper gives an overview on the electrical resistivity behaviour at temperature variations of most known transparent electrodes: ITO, FTO, AZO, PEDOT:PSS etc. It is well known that between the structural characteristics of thin films and their electronic transport properties there is a strong correlation. On this basis, the study of the temperature dependence of the electrical properties of thin films, may offer useful information about the possible changes of the structural characteristics of the films. Moreover, when this study is carried out during successive heating and cooling cycles, such structural changes can be revealed. In the case of transparent conducting films with applications in photovoltaic devices, the measurements of the electrical resistivity during many successive heating and cooling cycles may provide useful information on the thermal stability of the electrode and temperature limitations. Solar cells are subject of periodic variations of temperatures (day-night) due to their exposure to sun. This repetitive heating lead in many cases to modifications of the constitutive films physical properties.

In this paper we present an overview of the main characteristics of thin films used as electrodes in solar cells and their stability to temperature variations, from the electrical point of view.

2. EXPERIMENTAL

The electrical resistivities of different transparent conducting films such as: ZnO, ZnO:Al (AZO), ZnO:In (IZO), SnO_2, SnO_2:F (FTO), In_2O_3, In_2O_3:Sn (ITO), PEDOT:PSS single layers or ITO/Metal/ITO, or ZnO/Metal/ZnO three layers thin films, either commercial or prepared by different methods (sputtering, thermal oxidation, spin-coating, PLD) [7–20] were measured using a four-point probe system, during many cycles of heating and cooling.

3. RESULTS AND DISCUSSION

The electrical behaviours of different transparent conducting films as function of temperature are given in Figs. 2–7. The stoichiometric oxides materials are intrinsic semiconductors: their conductivity are not very high and their resistivity decreases with the temperature increasing as for all semiconductors. The conductivity is improved by doping and, if the doping level is not very high, we first have a decrease of the resistivity with the temperature due to the thermal activation transitions between the impurities levels and the conduction band. At very high doping levels the semiconductor becomes degenerate and the variation of the resistivity with the temperature is less pronounced (Fig. 2, ITO -1), however since the optical window length is depending on carrier concentration, very high doping levels lead to a reduction of the transparency domain. It is hence obviously that the electrical conductivity of oxide films will change with the temperature variations.

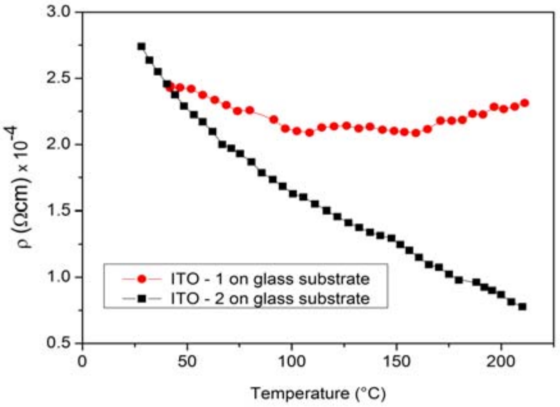

Fig. 2 – Electrical resistivity dependences as function of temperature for two commercial ITO thin films.

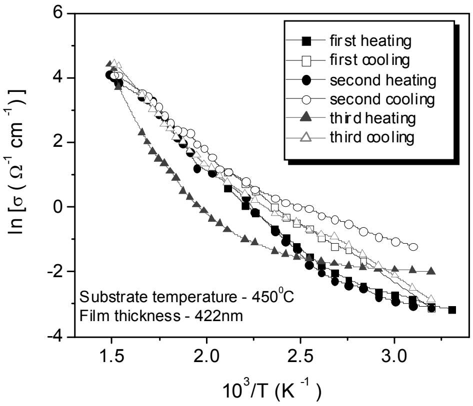

Fig. 3 – Plots of ln σ *vs.* 1000/*T* during three cycles of heating and cooling for FTO thin films. The heating temperature was 200°C for the first cycle and 400°C for the second and third cycles.

Generally the dependences of the resistivity on the temperature for the firsts heating – cooling cycles are not reversible. Films suffer irreversible modifications of the grains sizes or filling of oxygen vacancies [7, 21-22]. These dependencies may become reversible after many cycles of heating and cooling or thermal treatments, but, for non-degenerate semiconducting thin films, the resistivity will continue to decrease with the increase of temperature (Fig. 2–Fig. 5). This is not unfavourable for solar cells functioning, but that means that the devices characteristics change during their operation.

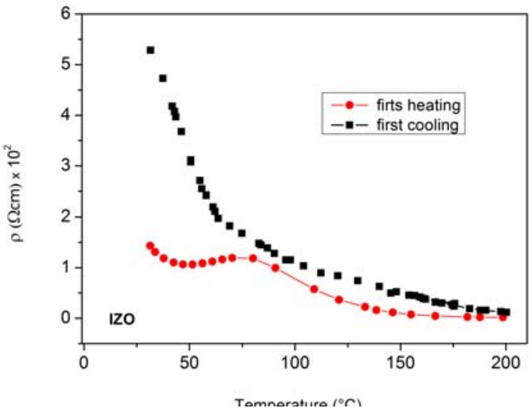

Fig. 4 – Electrical resistivity dependences as function of temperature during a heating- cooling cycle between 25 and 200°C, for an IZO thin film deposited by spin coating.

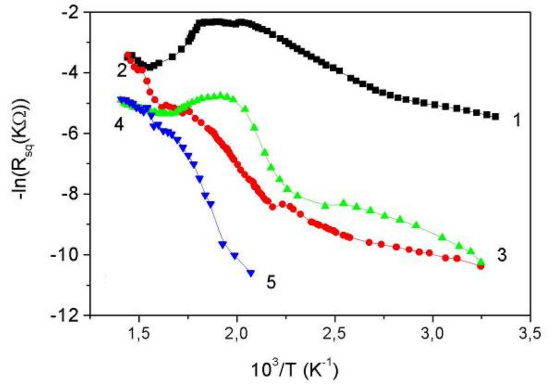

Fig. 5 – Plots of ln σ *vs*. 1000/*T* during two cycles of heating and cooling for a ZnO thin film prepared by thermal oxidation of metallic thin films.

The dependencies on the temperature of the conducting polymers PEDOT:PSS films are reproducible and reversible for many heating-cooling cycles from the beginning (Fig. 6). The resistivity also decreases with the temperature increase but it also decreases with the light intensity enhancement [13]. The modifications of electrodes electrical properties during the sun exposure of the devices (by temperature increasing and light exposure) may explain some of problems concerning the stability and reproducibility observed in the I-V characterization of third generation solar cells. Different from single layer transparent conducting films based only on semiconductor materials, the studies on the three-layer oxide/metal/oxide films, show very stable and reproducible values of the electrical resistivity (Fig. 7) to temperature variations.

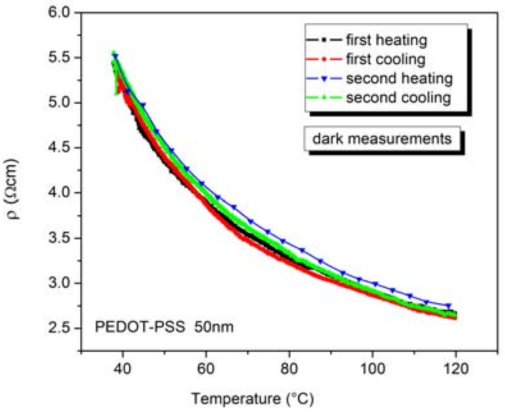

Fig. 6 – Electrical resistivity dependences as function of temperature during a heating - cooling cycle between 25 and 120°C for a PEDOT-PSS thin film deposited by spin coating.

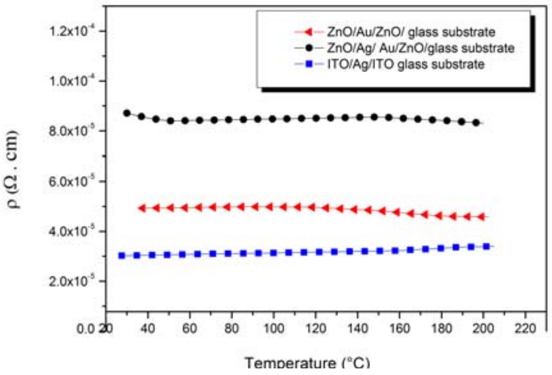

Fig. 7 – Electrical resistivity dependences as function of temperature during a heating - cooling cycle between 25 and 200°C for different oxide/metal/oxide three layers thin films deposited by sputtering.

That may be explained by the low dependence of the electrical conductivity of metals with temperature. A very precise metal thickness (about 7–8 nm) is necessary for these films in order to obtain a high transparency and high electrical conductivity [14]. The primary characteristics, namely, work function, band gap, roughness, and electrical stability of the main transparent conducting films as electrodes for the third generation solar cells, are given in Table 1.

Table 1

Main transparent conducting thin films used in the third solar cells architectures

Transparent conducting thin film	***Work function (eV)***	[Ref]	***Band gap (eV)***	[Ref]	***Roughness (nm) / deposition method***	[Ref]	***Electrical stability***
In_2O_3, In_2O_3:Sn (ITO)	4.1 - 5.5	[23]	3.5 - 3.7	[23]	2-10 nm / sputtering	[14]	weak /medium
SnO_2 , SnO_2:F (FTO)	4.2 - 4.4	[23]	4.0 - 4.5	[23]	40-20 nm / spray 12-17 nm / sputtering	[25] [26]	weak /medium
ZnO, ZnO:Al (AZO) ZnO:In (IZO)	4.3 - 4.4	[23]	3.2 - 3.6	[23]	40-90 nm / oxidation 4-20 nm / spin coating 8-18 nm / PLD 8-17 nm / sputtering	[19] [7] [16] [27]	weak weak
PEDOT: PSS	5.1	[24]	-		1-5 nm / spin coating	[13]	medium
ITO/Ag/ITO ZnO/Au/ZnO	4.85 4.80	[28] [28]	-		1-3 nm / sputtering 2-4 nm / sputtering	[28] [28]	high

4. CONCLUSIONS

The electrical resistivity behaviour at temperature variations was investigated for ZnO, ZnO:Al (AZO), ZnO:In (IZO), SnO_2, SnO_2:F (FTO), In_2O_3, In_2O_3:Sn (ITO), PEDOT:PSS single layers or ITO/Metal/ITO, or ZnO/Metal/ZnO three layers thin films prepared by different methods: sputtering, thermal oxidation, spin-coating, and PLD. For the single layer transparent conducting oxide films, the dependencies of resistivity with the temperature are, in the most of cases, irreversible. Reversible dependencies were obtained for the PEDOT-PSS conducting organic polymer films. Obviously, for the semiconducting single- layer films, except the case of high-doped (degenerate) semiconductors, the resistivity decreases with the increasing of the temperature. Stable values of the electrodes resistivity, in the temperature range of operating solar cells, were obtained for the oxide/metal/oxide three-layer films. These films are very smooth and their roughness is comparable to that one of commercial ITO films. Their work function, which is about 4.80–4.85 eV, evaluated according to [28], is also close to that one of ITO (about 4.1–5.5 eV).

ACKNOWLEDGMENTS

The authors are grateful to French Research Ministry for the financial support in the frame of European Project ERA-NET-RUS.

REFERENCES

1. N. S. SARICIFTCI, L. SMILOWITZ, A. J. HEEGER, F. WUDL, *Photoinduced electron-transfer from a conducting polymer to buckminsterfullerene*, Science, **258**, pp.1474–1476, 1992.
2. I-W. HWANG, J. Y. KIM, S. CHO, J. YUEN, N. COATES, K. LEE, M. HEENEY, I. MCCULLOCH, D. MOSES, A. J. HEEGER, *Bulk heterojunction materials composed of poly(2,5-bis(3-tetradecylthiophen-2-yl)thieno 3,2-b thiophene): Ultrafast electron transfer and carrier recombination,* Journal of Physical Chemistry C, **112**, pp.7853–7857, 2008.
3. M. GIRTAN, M. RUSU, *Role of ITO and PEDOT:PSS in stability/degradation of polymer: fullerene bulk heterojunctions solar cells*, Solar Energy Materials and Solar Cells, **94**, pp. 446–450, 2010.
4. A. RADU, S. IFTIMIE, V. GHENESCU, C. BESLEAGA, V. A. ANTOHE, G. BRATINA, L. ION, S. CRACIUN, M. GIRTAN, S. ANTOHE, T*he influence of lif layer and zno nanoparticles addings on the performances of flexible photovoltaic cells based on polymer blends,* Digest Journal of Nanomaterials and Biostructures, **6**, pp. 1141–1148, 2011.
5. S. IFTIMIE, A. RADU, M. RADU, C. BESLEAGA, I. PANA, S. CRACIUN, M.GIRTAN, L. ION, S. ANTOHE, *Influence of PEDOT:PSS layer on the performances of "bulk-heterojunction" photovoltaic cells based on MEH-PPV:PCBM (1:4) polymeric blends*, Digest Journal of Nanomaterials and Biostructures, **6,** pp. 1631–1638, 2011.
6. M. K. NAZEERUDDIN, M. GRÄTZEL, *Conversion and Storage of Solar Energy using Dye-sensitized Nanocrystalline TiO2 Cells*, in *Comprehensive Coordination Chemistry* II, E.-C. J. A. McCleverty and T. J. Meyer (Eds.), pp. 719–758, Pergamon, 2003.

7. M. GIRTAN, M. SOCOL, B. PATTIER, M. SYLLA, A. STANCULESCU, *On the structural, morphological, optical and electrical properties of sol-gel deposited ZnO In films*, Thin Solid Films, **519**, pp. 573–577, 2010.
8. M. GIRTAN, *Investigations on the optical constants of indium oxide thin films prepared by ultrasonic spray pyrolysis*, Materials Science and Engineering B-Solid State Materials for Advanced Technology, **118**, pp. 175–178, 2005
9. M. GIRTAN, A. BOUTEVILLE, G. G. RUSU, M. RUSU, *Preparation and properties of* SnO_2□*: F thin films*, Journal of Optoelectronics and Advanced Materials, **8**, pp. 27–30, 2006.
10. D. CHAPRON, M. GIRTAN, J. Y. LE POMMELEC, A. BOUTEVILLE, *Droplet dispersion calculations for ultrasonic spray pyrolysis depositions*, Journal of Optoelectronics and Advanced Materials, **9**, pp. 902–906, 2007.
11. G. G. RUSU, M. GIRTAN, M. RUSU, *Preparation and characterization of ZnO thin films prepared by thermal oxidation of evaporated Zn thin films*, Superlattices and Microstructures, **42**, pp. 116–122, 2007.
12. M. RUSU, G. G. RUSU, M. GIRTAN, S. D. SEIGNON, *Structural and optical properties of ZnO thin films deposited onto ITO/glass substrates*, Journal of Non-Crystalline Solids, **354**, pp. 4461–4464, 2008.
13. M. GIRTAN, R. MALLET, D. CAILLOU, G. G. RUSU, M. RUSU, *Thermal stability of poly(3,4-ethylenedioxythiophene)-polystyrenesulfonic acid films electrical properties*, Superlattices and Microstructures, **46**, pp. 44–51, 2009.
14. M. GIRTAN, *Comparison of ITO/metal/ITO and ZnO/metal/ZnO characteristics as transparent electrodes for third generation solar cells*, Solar Energy Materials and Solar Cells, **100**, pp.153–161, 2012.
15. M. GIRTAN, H. CACHET, G. I. RUSU, *On the physical properties of indium oxide thin films deposited by pyrosol in comparison with films deposited by pneumatic spray pyrolysis*, Thin Solid Films, **427**, pp. 406–410, 2003.
16. M. GIRTAN, M. KOMPITSAS, R. MALLET, I. FASAKI, *On physical properties of undoped and Al and In doped zinc oxide films deposited on PET substrates by reactive pulsed laser deposition,* Eur. Phys. J.-Appl. Phys., **51**, Art. No. 33212, 2010.
17. I. VAICIULIS, M. GIRTAN, A. STANCULESCU, L. LEONTIE, F. HABELHAMES, S. ANTOHE, *On titanium oxide spray deposited thin films for solar cells applications*, Proceedings of the Romanian Academy Series A-Mathematics, Physics Technical Sciences, Information Science, **13,** pp. 335–342, 2012.
18. M. GIRTAN, A.VLAD, R. MALLET, M.A. BODEA, J.D. PEDARNIG, A. STANCULESCU, D. MARDARE, L. LEONTIE, S. ANTOHE, *On the properties of Aluminium doped Zinc Oxide thin films deposited on plastic substrates from ceramic targets*, Applied Surface Science, **274,** pp. 306-313, 2013.
19. M. GIRTAN, G.G. RUSU, S. DABOS-SEIGNON, M. RUSU, *Structural and electrical properties of zinc oxides thin films prepared by thermal oxidation*, Applied Surface Science, **254,** pp. 4179–4185, 2008.
20. M. GIRTAN, *The influence of post-annealing treatment on the electrical properties of in2o3 thin films prepared by an ultrasonic spray CVD process*, Surface & Coatings Technology, **184,** pp. 219–224, 2004.
21. M. GIRTAN, G.I. RUSU, G.G. RUSU, S. GURLUI, *Influence of oxidation conditions on the properties of indium oxide thin films*, Applied Surface Science, **162,** pp. 492–498, 2000.
22. M. GIRTAN, G.I. RUSU, G.G. RUSU, *The influence of preparation conditions on the electrical and optical properties of oxidized indium thin films*, Materials Science and Engineering B-Solid State Materials for Advanced Technology, **76,** pp. 156–160, 2000.
23. H.L. HARTNAGEL, A.L. DAWAR, A.K.C. JAIN, JAGADISH, S*emiconducting, transparent thin films*, IOP Publishing Ltd., 1995.
24. M. NARDES, M. KEMERINK, M.M. DE KOK, E. VINKEN, K. MATUROVA, R.A.J. JANSSEN, *Conductivity, work function, and environmental stability of PEDOT:PSS thin films treated with sorbitol,* Organic Electronics, **9**, pp. 727–734, 2008.
25. SUK IN NOH, HYO-JIN AHN DOH-HYUNG RIU, *Photovoltaic property dependence of dye-sensitized solar cells on sheet resistance of FTO substrate deposited via spray pyrolysis,* Ceramic International, **38**, *5*, pp. 37353739, 2012
26. S.-J. LIU, L.-Y. CHEN, C.-Y. LIU, H.-W. FANG, J.-H. HSIEH, AND J.-Y. JUANG, *Physical properties of polycrystalline Cr-doped SnO2 films grown on glasses using reactive dc magnetron co-sputtering technique*, Applied Surface Science, **257**, *6*, pp. 2254–2258, 2011.
27. W-H YAU, P-C TSENG, D. LIAN, *Nanoscratch study of ZnO thin films deposited using radio frequency magnetron sputtering*, Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions With Materials and Atoms, **269**, *12*, pp. 1450–1454, 2011.
28. M. GIRTAN, *On the stability of the electrical and photoelectrical properties of p3ht and P3HT:PCBM blends thin films*, Organic Electronics, **14,** pp. 200–205, 2013.

Received December 10, 2013