

Comparison of different conducting oxides as substrates for CdS/CdTe thin film solar cells

N. Romeo^a, A. Bosio^{a,*}, V. Canevari^b, M. Terheggen^c, L. Vaillant Roca^d

^aUniversità degli Studi di Parma, Dipartimento di Fisica, INFN – Istituto Nazionale di Fisica della Materia, Parco area delle Scienze 7/A, I-43100 Parma, Italy

^bIMEM – CNR, Parma, Italy

^cETH Zurich, Institute of Applied Physics, 8093 Zurich, Switzerland

^dFacultad de Fisica – IMRE, Universidad de La Havana, 43100 La Havana, Cuba

Abstract

A study of several types of transparent conducting oxides (TCO) is reported. In particular we have investigated the interaction between the TCO and CdS layers from the point of view of the completed CdS/CdTe solar cell parameters in respect to the deposition parameters of the TCO films. All different TCO films are deposited by sputtering in pure argon or in argon + hydrogen, Ar + CHF₃, argon + Oxygen. The kinds of TCO studied are: tin doped In₂O₃, fluorine doped In₂O₃, Cd₂SnO₄, germanium doped In₂O₃ (IGO), SnO₂, and Zn₂SnO₄. The devices are fabricated with a single TCO layer, i.e. fluorine doped In₂O₃, or in a double layer configuration, i.e. IGO covered by SnO₂. We have found that the performance of the device depends strongly on the interaction between the surface of the TCO and the CdS film. This interaction derives overall from the stability of the Oxygen atoms on the surface of the TCO films. This fact is clarified observing the behavior of the cells performance: the device is better if the TCO layer in contact with the CdS film is deposited in Ar+H₂ atmosphere. The best CdS/CdTe solar cells, with an efficiency of approximately 14%, are obtained by using 0.4 μm of fluorine doped In₂O₃ as a TCO. The sputtering atmosphere used for the deposition of this kind of TCO is a mixture of Ar, Ar+H₂ and CHF₃.

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Keywords: Film; Transparent conducting oxides; Photovoltaic; CdTe

1. Introduction

The technology of the CdTe/CdS thin film solar cells through intense studies at universities, institutes and industrial groups has reached a stage, where the transfer into production is generally considered to be appropriate. This means that every single layer which form the device is almost completely understood both from the point of view of its chemi-physical behavior and from the point of view of the deposition techniques. For example cadmium sulfide (CdS) has been found to be the best-suited material for thin film CdTe heterojunction solar cells, and conversion efficiencies higher than 16% [1,2] have been reported for CdS/CdTe solar cells prepared by several techniques. In efficient solar cells, CdS films are prepared by RF sputtering, close-spaced sublimation (CSS) and chemical-bath-deposition and

CdTe films are deposited by CSS, electrodeposition and metal-organic chemical vapor deposition. Each technique has its own merits but in particular, in order to realize a device easily scalable for industrial needs (i.e. the costs of the equipment, the deposition rate and the final cell performance) the CSS and sputtering techniques seem to be best-suited. Despite these remarkable points, the preparation of thin film solar cells based on CdTe/CdS heterojunction still exhibits quite a few open problems and it is therefore subjected to a great margin of progress. One of the open questions, definitively resolved in our laboratory, is certainly the back contact, which is crucial for the temporal stability of the solar cell. In fact in order to realize a low resistance, possibly ohmic contact with p-type CdTe film, use is made of various metals like Cu, Hg, Pb or Au which, due to their ability of diffusing into the different layers may deteriorate the device. We solved the back contact problem by depositing a thin layer of Sb₂Te₃, which is a stable compound that exhibits a forbidden energy gap

*Corresponding author. Tel.: +39-521-905257; fax: +39-521-905223.

E-mail address: alessio.bosio@fis.unipr.it (A. Bosio).

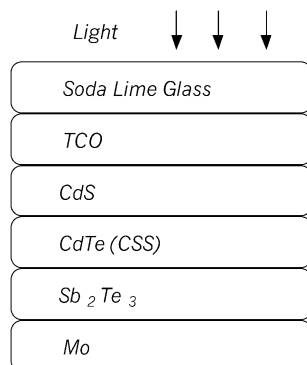


Fig. 1. Schematic of the CdTe/CdS solar cell.

of 0.3 eV and is a degenerate p-type semiconducting material with a resistivity of $10^{-4} \Omega \text{ cm}$. The Sb_2Te_3 layer is deposited by sputtering at a substrate temperature of 300–350 °C. This high substrate temperature allows the formation of a p+ Sb_2Te_3 layer on top of CdTe film which assures, together with its low resistivity, the ohmic behavior of the back contact. Another open question is the presence, in the positive part of the CdTe/CdS thin film solar cell current–voltage (I – V) characteristic [3], of the so called ‘roll-over’ (in this region the dark and light I curves intersect themselves into a point near the V axis). We demonstrated that this behavior in the I – V characteristic cannot be attributed only to a rectifying or not ohmic back contact but strongly depends on the way the front contact is made. Having resolved the problem of the stability of the back contact, we found out that an instability in the cell can rise from the front contact, namely the transparent conducting oxide (TCO). The aim of this work is to give an answer to this problem. In order to do that we studied several kind of TCOs and their interaction with the CdS layer deposited on top of them from the point of view of the final behavior of the device.

2. Experimental procedure

2.1. Solar cell structure

The structure of the solar cell studied in this paper is shown in Fig. 1. We prepared efficient thin film CdTe/CdS solar cells by using CdS films deposited via the RF sputtering technique and CdTe films deposited by CSS, both low-cost scalable techniques. Our CSS apparatus is in detail described in Ref. [4]. The device is in the front-wall configuration, i.e. films of CdS, p-type CdTe, and an ohmic back contact are subsequently deposited onto a TCO coated soda-lime glass. The back contact on CdTe film is made by depositing in sequence at a substrate temperature of 300–350 °C, 1500 Å of Sb_2Te_3 and 1500 Å of Mo films. Both materials are deposited by RF sputtering with a deposition rate greater

than 10 Å/s. CdTe films are deposited by CSS at a substrate temperatures in the range of 480–540 °C while the CdTe source is kept at approximately 650 °C. During the deposition, the argon partial pressure is 1 mbar and the distance between the source and the substrate is approximately 4 mm. The typical deposition rate is 2 $\mu\text{m}/\text{min}$ and the requested time for the film preparation is 3–4 min. CdS films are prepared with a typical deposition rate of 10 Å/s by means of a partial argon pressure in the sputtering chamber of 10^{-3} mbar. The substrate temperature is 300 °C and the final thickness of the CdS films is 1000 Å. During our investigations we found out that independently from the type of TCO the system formed by soda-lime glass covered by TCO and CdS film needs to be annealed in air in order to obtain high efficient devices. The annealing temperature and time are, respectively, approximately 500–520 °C and 20 min. During the annealing in air, there is an interaction between the soda-lime glass, the TCO and CdS films, which is showed by the presence on top of CdS of a thin layer of a new material that is a reaction product. This material is soluble in hot water and must be removed before the deposition of the CdTe film [5]. The results of X-ray photoelectron spectroscopy (XPS) carried out on this material are shown in Fig. 2. The oxygen 1s signals at binding energies of 532.5, 530 and 529 eV correspond to CdSO_4 , In_2O_3 and CdO, respectively. From these results we deduce that the material which is formed on top of CdS is constituted by two layers namely CdSO_4 with a thickness within 20–60 Å and CdO with a thickness within 300–500 Å. Presumably the thickness of CdSO_4 and CdO layers depends both on annealing temperature and time. The amount of these layers also depends on the presence of Na and then on the thickness of both TCO and CdS films. The annealing in air at the same temperature of a CdS film deposited onto alkali-free glass did not show the formation of any material on top of CdS film indicating that the TCO and Na are needed for it to be formed. After the annealing in air we observed the formation of this material, with different thickness, on top of CdS film with all the TCOs checked in our laboratory. From this point of view the choice of the TCO is very important for the preparation of the CdTe/CdS solar cells not only for its electro–optical characteristics but especially, for its interaction with CdS.

2.2. The TCO layers

In this work several types of TCO are studied; all the TCO thin films are deposited by RF sputtering at 500 °C substrate temperature and the deposition rate is typically in the range of 5–10 Å/s. Cerac Inc. supplied all the different TCO’s sputtering targets. They are 3 inch in diameter sized and made by the hot-pressing technique.

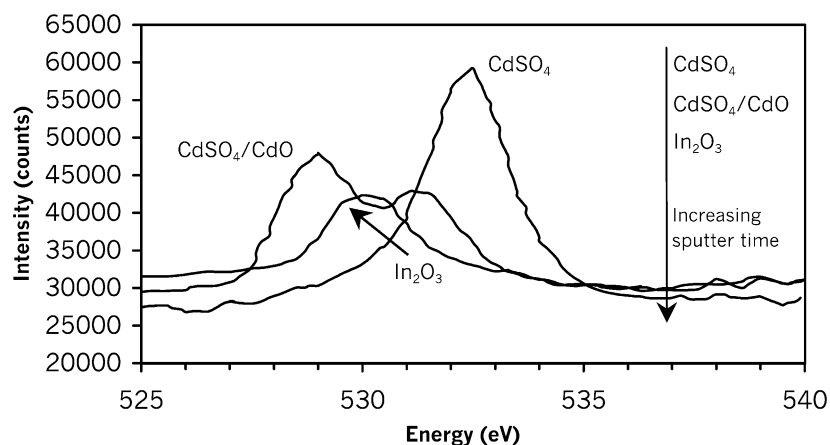


Fig. 2. XPS made on top of TCO/CdS double layer after air annealing at 520 °C.

Tin doped In_2O_3 (ITO) films were obtained by RF sputtering from different targets with different stoichiometries; in particular we studied four kind of ITO: In_2O_3 containing, respectively 1, 2, 4 and 10% weight of SnO_2 . ITO films were prepared by using the reactive-sputtering deposition, which consists to put into the sputtering chamber a little amount of reactive gas together with the argon sputtering gas. Some ITO films were deposited in a sputtering gas mixture containing $\text{Ar} + \text{O}_2$; the O_2 partial pressure was varied between 2 and 20% in respect to $\text{Ar} + \text{O}_2$ total pressure. Other ITO films were prepared in a gas mixture containing $\text{Ar} + \text{H}_2$; the H_2 partial pressure was changed in the range of 1–10% in respect to $\text{Ar} + \text{H}_2$ total pressure. All these films exhibit a very low resistivity of $2 \times 10^{-4} \Omega \text{ cm}$; the resistivity of the ITO films does not depend on the stoichiometry of the target and on the amount and type of the reactive gas used during the sputtering deposition. This probably means that Sn is an effective dopant and the doping level does not depend on oxygen vacancies. The films are enough transparent to be used as front contact for CdTe/CdS solar cells. The stability of the ITO layers is better for films prepared in $\text{Ar} + 4\% \text{H}_2$ gas. In fact, after the annealing in air of the soda-lime glass/ITO/CdS system at a temperature over 520 °C, only a little amount of CdSO_4 and CdO was observed while, under the same annealing conditions, ITO films deposited in $\text{Ar} + \text{O}_2$ gas mixture presented a very thick CdSO_4/CdO layer on top of CdS film. From the stability point of view we did not observe any benefit by covering the ITO films with SnO_2 . The amount of this reaction product depends also on the thickness of the TCO film and is less for the thicker ITO films. This fact is probably due to a better shield against Na diffusion from the soda-lime glass. However, we found out that the efficiency of the solar cells, by using an ITO film thicker than 1.2 μm , could be quite high (above 14%) but was not much reproducible. We explain this consid-

ering that all the ITO targets modify their surface after several runs forming some In-rich nodules which can cause some occasional discharges during the sputtering deposition [6]. This discharge instability produces a not stoichiometrically uniform ITO film. Fluorine doped tin-oxide was prepared by using a target of SnO_2 . The film was doped by mixing the Ar sputtering gas with CHF_3 in the range 1–20% in respect to the total $\text{Ar} + \text{CHF}_3$ gas pressure. The minimum resistivity that we were able to obtain by making use of the maximum quantity of CHF_3 in the sputtering chamber during the SnO_2 deposition is approximately $8 \times 10^{-4} \Omega \text{ cm}$. The SnO_2 film transparency was not as high as that of the ITO film. A disadvantage in comparison with the ITO films is the resistivity of the $\text{SnO}_2:\text{F}$ that is 3–4 times greater. This means that in order to obtain the same sheet resistance as that of the ITO layer we are forced to deposit a $\text{SnO}_2:\text{F}$ film 3–4 times thicker losing the transparency. As a consequence we did not prepare any solar cell with $\text{SnO}_2:\text{F}$ alone but we used this material as a buffer layer. For example we deposited a $\text{SnO}_2:\text{F}$ film, 1000–5000 Å thick on top of an ITO film prepared as described above. The final performance of the solar cell did not change in comparison with the device fabricated by making use of ITO alone. Germanium doped indium oxide (IGO) films were prepared by RF sputtering from a target of In_2O_3 containing 4% weight of GeO_2 and the typical deposition rate was larger than 10 Å/s. The surface of this target did not present any formation of In-rich nodules and the film deposition was much stable and reproducible. The preparation of IGO film was carried out by using pure argon or a mixture of Ar, H_2 and CHF_3 as sputtering reactive gas. In the first case we obtained an IGO film with a resistivity on the order of $5 \times 10^{-4} \Omega \text{ cm}$ and a very good transparency in the visible region of the spectrum [7]. This means that germanium has the same behavior of tin into In_2O_3 matrix and results to be an effective dopant for In_2O_3 .

The IGO film deposited by reactive-sputtering by using a mixture of $\text{Ar} + \text{H}_2 + \text{CHF}_3$ as sputtering gas presented a resistivity of $2 \times 10^{-4} \Omega \text{ cm}$. This result shows that hydrogen could create some oxygen vacancies into the In_2O_3 matrix giving more possibility to the fluorine substitute oxygen and therefore can dope better the IGO film during the deposition. The H_2 and CHF_3 gas pressure were, respectively 2 and 5% in respect to the total $\text{Ar} + \text{H}_2 + \text{CHF}_3$ gas pressure. The IGO films showed a good stability in respect to the air annealing of the TCO/CdS system at a temperature of 520°C since we observed a very little amount of CdSO_4/CdO on top of CdS film after the air annealing. The IGO film stability and its very low resistivity allowed us to use, as a TCO layer, only a 4000 \AA thick film. With this TCO we fabricated solar cells with efficiency up to 14% and a very good reproducibility. Zn_2SnO_4 and Cd_2SnO_4 thin films were prepared by reactive RF sputtering. The sputtering gas was a mixture of $\text{Ar} + 50\% \text{O}_2$. Both the materials are very transparent exhibiting a transparency larger than 90% in the wavelength range between 400 and 850 nm. Zn_2SnO_4 thin films showed a resistivity on the order of $10^{-2} \Omega \text{ cm}$. This resistivity is too high for Zn_2SnO_4 films to be used in solar cell production. We tried to dope Zn_2SnO_4 by reactive-sputtering with CHF_3 but, unfortunately fluorine did not result an effective dopant in this material; probably, the presence of oxygen during the sputtering deposition, inhibits fluorine atoms to enter into Zn_2SnO_4 matrix. The preparation of Cd_2SnO_4 thin films was carried out with the same sputtering parameters of the Zn_2SnO_4 deposition and the resistivity of these films was on the order of $2 \times 10^{-4} \Omega \text{ cm}$ that is comparable with the resistivity of the best ITO and IGO films. In reason of its high transparency and conductivity this material seems to be quite suitable to realize high efficiency CdTe/CdS solar cells [8]. However, the sputtering target, since it is made by a hot pressed mixture of CdO and SnO_2 powders, being CdO hygroscopic, is difficult to be handled. Due to this fact, the target is not sufficiently stable and in order to avoid some damage the sputtering power density must be kept very low. As a consequence, the deposition rate was $\leq 2 \text{ \AA/s}$. Since this material is highly hygroscopic, we found out some problems when we put the soda-lime glass covered by $\text{Cd}_2\text{SnO}_4/\text{CdS}$ into the oven in order to make the annealing in air at a 520°C temperature. In some cases the CdSO_4/CdO formation is very consistent. This fact is probably due to the instability caused by the absorption of water from the Cd_2SnO_4 film. Despite this, by depositing 4000 \AA of Cd_2SnO_4 covered by 1000 \AA of CdS onto soda-lime glass and then processing this system in air in our usual way, we were able to obtain highly efficient solar cells. The best cell performance is, in this case, comparable with that of the cells fabricated by using IGO as a TCO layer. Last TCO was

fluorine doped indium oxide layer (INO). In_2O_3 can be sputtered at a relatively high deposition rate ($\geq 10 \text{ \AA/s}$) without any change on the target surface. When In_2O_3 is not intentionally doped during the sputtering deposition it grows with a resistivity on the order of $10^{-2} \Omega \text{ cm}$. In this case the conductivity is due to native defects, such as oxygen vacancies. We were able to prepare INO films with a resistivity of $2.5 \times 10^{-4} \Omega \text{ cm}$ introducing Ar containing 5% of H_2 and 5% of CHF_3 in the chamber during the sputtering deposition. The INO films obtained in this way are very smooth and transparent. Besides, we found out that 1000 \AA of this material are sufficient to passivate sodium atoms which can diffuse into the film from the soda-lime glass. For this reason and for its intrinsic stability, INO is perhaps, the best-suited material for solar cells production. In fact, we always observed a very little amount of CdSO_4/CdO when we annealed this TCO covered by CdS at 520°C in air. Depositing 4000 \AA of INO and 1000 \AA of CdS onto 1 inch^2 soda-lime glass and after the usual stabilization in air of the system, we obtained a CdTe/CdS solar cell with the following parameters:

$$V_{\text{oc}} \approx 848 \text{ mV} \quad \text{ff} \approx 0.65$$

$$J_{\text{sc}} \approx 25.4 \text{ mA/cm}^2 \quad \eta \approx 14\%$$

where V_{oc} is the open-circuit voltage, J_{sc} is the short-circuit current density, ff is the fill factor and η is the efficiency of the solar cell. The different characteristics of the TCOs are summarized in Table 1.

3. Conclusions

The cells fabricated without antireflection coating, with an area of approximately 1 cm^2 by making use of 1 inch^2 soda-lime glass covered by the different types of TCO previously described, exhibit a very good device efficiency, on the order of 14%. The J vs. V characteristics were tested in the dark and under illumination and the photovoltaic parameters were measured under the standard condition of 300 K, 100 mW/cm^2 and AM1.5 by using a solar simulator supplied by Oriel Inc. The best results are obtained by using an INO thin film, 4000 \AA thick, as a front contact. This is a very satisfactory result overall in respect to the reproducibility and time-stability of the solar cell. In fact, after the usual air annealing of the INO–CdS system at a temperature of 520°C , we are always able to obtain a solar cell that improve its efficiency by making a light-soaking of 20 h under ten suns at 110°C (in the open-circuit voltage conditions). In a lot of cases the efficiency is higher after aging. We believe that this high stability is due to both the use of Sb_2Te_3 as back contact and the CdS stabilization with a possible CdS grain boundary passivation after the high temperature air annealing. The

Table 1

Characteristics of the TCOs used as front contacts for the CdTe/CdS solar cells

TCO	Sputtering gas	Resistivity (Ω cm)	Transparency 400–800 nm	Stability of the device ^a	Reproducibility
ITO	Ar+4% H_2	2×10^{-4}	$\geq 80\%$	Good	Good
SnO ₂	Ar+20% H_2	8×10^{-4}	80%	–	–
IGO	Ar+CHF ₃ + H_2	2×10^{-4}	85%	Very good	Very good
Cd ₂ SnO ₄	Ar+50%O ₂	2×10^{-4}	85%	Very good	Very good
Zn ₃ SnO ₄	Ar+50%O ₂	10^{-2}	$\approx 90\%$	–	–
INO:F	Ar+CHF ₃ + H_2	2.5×10^{-4}	$\geq 85\%$	Excellent	Excellent

^a Stability of the CdTe/CdS solar cell made on different TCO after the aging process in the ‘open-circuit conditions’, under 10 suns, at a temperature of 110 °C for 20 h.

only limiting parameter in these cells is the fill factor since there is a roll-over in the positive part of the J – V characteristic. This is probably due to a partially compensation of the p-type carriers in the middle zone between the junction and the back contact inside the CdTe film. This compensation could depend on the purity of the starting CdTe material.

Acknowledgments

The authors gratefully acknowledge Prof. G. Kostorz from ETH Zurich, Institute of Applied Physics, 8093 Zurich and Dr Hauert from EMPA in Dübendorf for their scientific support with XPS measurements.

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