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The role of copper in bifacial CdTe based solar cells

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Abstract. We present an innovative back contact for CdTe solar cell by the application of a transparent conducting oxide, typically ITO, as a back electrical contact on CdTe/CdS photovoltaic devices that acts as a free-Cu stable back contact and at the same time allows to realize bifacial CdTe solar cells, which can be illuminated from either or both sides. The controlled insertion of a very limited amount of copper into the ITO back contact permits to have reproducible devices with high efficiencies still keeping the bifacial configuration. Thin CdTe layer solar cells with ITO back contact have been realized with efficiencies exceeding 10%, the reduced thickness of CdTe allows to have a better performance on the back-side illumination and reduces the amount of CdTe material.

Keywords: bifacial solar cells, front illumination, back illumination, efficiency, thin film.

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1. Introduction

At the moment First Solar company has realized a 75 MW production plant in USA and is about to set up a production plant of 100 MW in Germany. At the same time, the investigations directed to development of new types solar cells (SCs) on the CdTe film basis are continued. Among such SCs are the so-called bifacial solar cells. One of the main problems in this direction is connected with development of a transparent and stable electrical contact for *p*-CdTe. The development of an efficient and long-term stable electrical contact to *p*-type CdTe is difficult because of both the high electron affinity and high energy band gap of CdTe. Typically, a quasi-ohmic contact to *p*-type CdTe is obtained by chemical etching the CdTe surface in either bromine-methanol or nitric-phosphoric (NPH) acid etchant followed by the deposition of very thin buffer metal (Cu, Ni, Sb, etc.) or metal-chalcogenide (Cu_xTe, Sb₂Te₃, ZnTe, HgTe, etc.) layer. Finally, a metal layer (Mo, Au, Al, etc.) is deposited [1]. The best results with “non-Cu containing” contacts were obtained for Sb₂Te₃/Mo system [2]. The effect of copper on the SCs properties is complicated. On the one hand, the copper forms a quasi-ohmic contact with an increasing concentration of copper

into CdTe leads to degradation of the solar cell parameters (see, for example [3, 4]).

In this paper, we present the development of bifacial thin film solar cells on a glass substrate with rear copper-containing contacts of new type. The properties of the contacts and parameters of the SCs with these contacts were studied.

2. Fabrication and testing of solar cells

All the layers were grown by PVD methods. Commercially available soda-lime glass coated with fluorine doped tin oxide (FTO) was used as a substrate. CdS layer was grown in a high-vacuum evaporation chamber at the substrate temperature 150 °C. CdTe layer was then deposited at the substrate temperature close to 300 °C in the same chamber without breaking the vacuum. After that, the so-called “chloride” treatment was performed. The procedure included deposition of CdCl₂ layer with the thickness 400 to 600 nm onto CdTe surface followed by thermal annealing in air at 430 °C for 30 min. The standard back contact was made by evaporating Cu/Au after bromine-methanol treatment of the CdTe surface, followed by a short annealing at 200 °C in air. Standard solar cells have a typical efficiency value from 11 to 12% [5]. Some of the cells

were subjected to light illumination in a special chamber. The treatment of the SCs was performed under conditions of open circuit. The SCs were illuminated by the 500-W tungsten lamp, and the SC temperature was 80 °C. This accelerated treatment simulates operation of SCs during long time, and the time of measurements corresponded to 0.81, 1.62, 2.43, 3.78, 4.56, 5.4, 5.94, and 8 years. The measurements were carried out in Switzerland technological institute (Zürich). Therefore, in Figs 1 and 2 there are two scales and the bottom one corresponds to real time of testing, while the top one to estimated time of the SC operation under illuminating intensities 100 mW/cm².

3. Copper free bifacial cells

The bifacial devices are fabricated exactly in the way as the standard devices are made, the difference is exclusively in the back contact. We have introduced a new approach to apply a transparent back contact on CdTe solar cells: after bromine-methanol etching the CdTe surface a thin layer of transparent and conducting ITO is sputtered and short annealing treatment in air is applied in the end. The conductivity of the ITO layers on glass has been measured as being about 15 Ohm/□, the layer has a sufficient transparency. Due to the transparency of the ITO back contact and FTO front contact, the solar cell can be illuminated both from the front and rear sides like a bifacial solar cell. As-deposited solar cells with a pure ITO back contact perform typically very low efficiencies around 2.5% against regular 12.5% efficiency with traditional back contact, in particular, V_{oc} and fill factor (FF) are extremely low. The change of these SC output parameters after the back contact post-deposition annealing is shown in Table 1. As a result of an annealing after ITO deposition, the V_{oc} , FF and short circuit current density J_{sc} increases, however, efficiency and after an annealing does not exceed 5%.

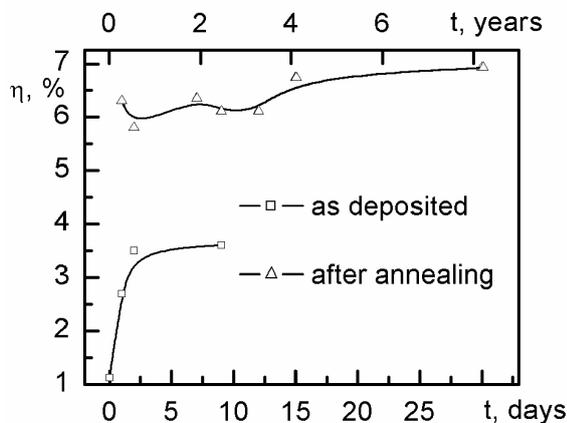


Fig. 1. Accelerated lifetime stability tests of an ITO/CdTe/CdS/FTO solar cell (before and after annealing at 350 °C).

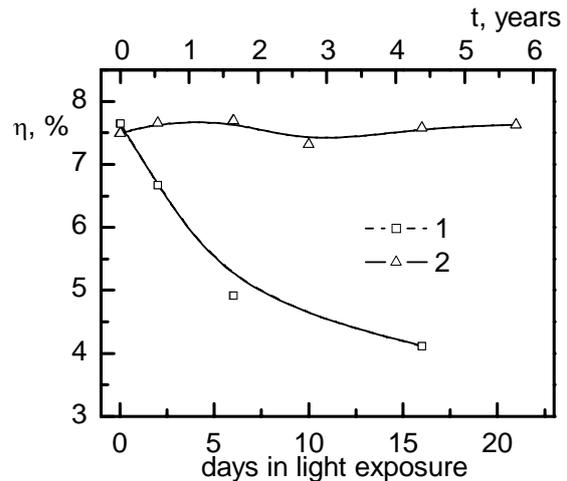


Fig. 2. Accelerated lifetime stability test of ITO/Cu/CdTe/CdS/FTO solar cells with 3 nm copper deposition (1) and less than 0.5 nm copper deposition (2).

It is logical to assume that, as the SC has a different only back contact, the difference of performance can be due to missing the buffer layer that allows tunneling of the carriers through the contact. To realize the dramatic difference between the traditional Cu-Au contact and the ITO contact properties, we have analyzed the fabrication process of the first one (Table 2). The main observation is the change of the device parameters before and after the back contact post-deposition annealing, the efficiency of the solar cells jumps from a poor value up to 10% efficiency as shown in Table 2. It can be stipulated by crystallization of tellurium containing layers on a back contact. The layers may appear after etching the base layer and (or) diffusion of copper into CdTe, which gives in its additional doping.

Table 1. Typical output parameters for SC with the ITO back contact.

SC output parameters	As-deposited	Annealed at 200 °C
V_{oc} (mV)	367	502
J_{sc} (mA/cm ²)	18.4	21.1
FF (%)	36.2	44
η (%)	2.4	4.6

Table 2. Typical output parameters of SC with the Cu/Au back contact.

SC output parameters	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	η (%)
As-deposited	322	12.2	40.45	1.6
Annealed 200 °C	723	22.2	54.4	8.8
Light-exposed	825	22	65	11.8

Various cells were prepared and after ITO RF sputtering, annealing in air annealed at different temperatures from 200 up to 400 °C, best results were given with annealing around 350 °C. The results are that from a starting efficiency of 1-2% and after annealing jumps to 4-5% that can still rise to an upper efficiency above 6% under light exposure. The increase in the efficiency is not the same as in the case of Cu/Au back contact, but the annealing is however improving the back contact, suggesting that the heating of the device after bromine-methanol etching re-crystallizes the Te rich layer.

The interesting feature of these solar cells is the stability under accelerated lifetime test, we have performed preliminary test also on these devices (solar cells were kept under AM1.5 illumination and at 80 °C temperature under open circuit conditions) and they presented an excellent stability and the performance actually improves instead of degrading (see Fig. 1).

The light exposure effect is different in cases of as-deposited and annealed devices: in the as-deposited device, the improvement is of the order of 200% for the first days (from about 1% efficiency up to above 3% efficiency) and successively tends to stabilize. In the annealed devices, the improvement is lower but still there is a stable increase in an almost ten year estimated operation time. It is clear that the defects at the junction between ITO and CdTe are clearly more in the as-deposited case and the light exposure fills the recombination centers at the junction, while in case of the annealed device the hetero-junction has a better quality and probably the crystallized Te layer helps to inject the carriers across the junction.

To reach typical efficiencies of a CdTe cell above 10% seems that the influence of copper is then fundamental as mentioned also by [6].

4. Copper containing bifacial cells

To have a complete panorama and in order to compare the SCs with ITO contacts with the standard copper-gold ones, we have analyzed the possibility of inserting copper into the back contact and to study the effects in the performance and in the stability. The basic principle is that a small amount of the copper would still leave the back contact transparent and, at the same time, might not affect the stability of the solar cell.

Several different devices have been made with a standard fabrication process but with different thickness of the copper film deposited onto SC prior to ITO deposition. Every cell has been processed with half area shadowed from the copper deposition in order to compare the different cells. Fig. 2 shows results of accelerated lifetime stability tests of cells with different amount of copper. One can see that initial efficiencies for both SCs are practically the same but the stability trend is opposite. The 3-nm Cu cell has a degradation that tends to stabilize after 4 years hypothetical time, is similar to the one observed for Cu/Au [7] but still the stability is higher, most probably due to the one order of magnitude less

amount of copper as compared to the standard cells (80 nm Cu). On the other hand, the <0.5nm-Cu cell starts from the same efficiency, but instead of degrading it improves slightly in the performance at the beginning of the light exposure and a successive stabilization as a very similar behavior of Sb₂Te₃/Mo cell [2].

For the back-side illumination, efficiencies have been in the order of 0.5% with V_{oc} of about 300 mV, J_{sc} of 3-4 mA/cm² and fill factor of 45%. The low current in the back-side illumination is due to the long distance between the hole-electron pair generation and the junction. We believe that if a stable compound with Cu is formed, then the back contact could be very stable, in particular what could happen is that after the creation of a thin layer of tellurium due to the bromine-methanol etching the copper reacts with the tellurium giving place to copper telluride that is a stable compound.

The proof for stability comes also from the annealing test made successively on the light exposed cells, annealing on these devices has been performed for 25 min at 300 °C. The annealed cells did not actually degrade, but instead their efficiency was improved in general by about 20% from a starting efficiency of 7.5% the efficiency of 9.2% was reached. The calculation of diode parameters has shown that the increase in efficiency is related to increase of shunting resistance and lowering the diode saturation current, at the same time, it is necessary to mark that after annealing the series resistance is grown.

5. Bifacial cells with a thin base layer

In order to improve the performance in the back-side illumination, we tried to reduce the distance between the junction and the electron-hole pair generation zone by reducing the thickness of the CdTe layer. The solar cell fabrication process has been adjusted to the different CdTe thicknesses, in particular the CdCl₂ treatment has been processed with only 20% of the standard CdCl₂ quantity and by reducing the annealing time.

The first cells were made with about 2.7 μm CdTe thickness and the most performing quantity of copper (0.5 nm). The solar cells started with a very good performance from the beginning as shown in Fig. 3a and increased after light exposure to reach the efficiency of 10% with $V_{oc} = 713$ mV, $J_{sc} = 19.3$ mA/cm², $FF = 73\%$.

The back-side illumination performance improved considerably compared to the standard cell, as shown in Fig. 3b after 3-day light exposure we have 2.1% with $V_{oc} = 659$ mV, $J_{sc} = 8.8$ mA/cm² and $FF = 36\%$, i.e., slight degradation follows. The stability of these cells is shown in Fig. 4, the cells are practically stable having a strong increase at the beginning and a successive slow degradation afterwards.

6. Bifacial cells with an ultra-thin base layer

Further lowering the CdTe layer thickness could open up different possibilities. First of all, there should be a

further increase in the back-side illumination performance, second, the solar cell becomes semi-transparent and could be used for tandem-configuration cells, and third, a mirror on rear side could be applied in order to absorb the light with energy close to the material band gap. Besides, in this case, a very low amount of material is used.

One micrometer CdTe thick solar cells were prepared using even more reduced CdCl₂ treatment, 30-nm thick CdCl₂ and 15 min annealing in air at standard annealing temperatures, copper insertion was reduced to less than 0.3 nm.

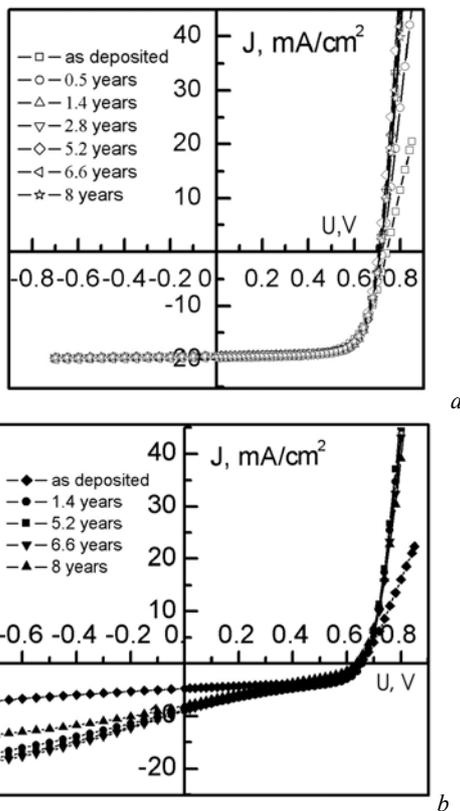


Fig. 3. *I-V* characteristic front-illuminated (a) and back-illuminated (b) 2.7- μm CdTe.

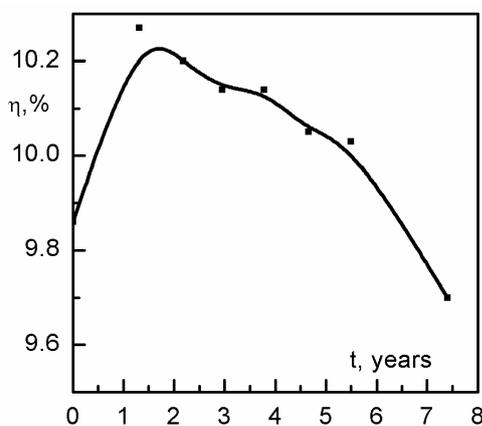


Fig. 4. Stability of thin absorber solar cells.

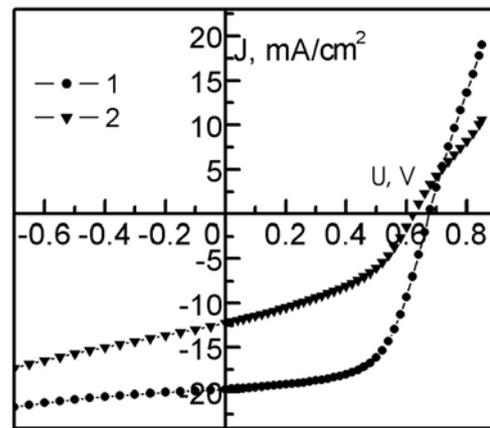


Fig. 5. *I-V* characteristic CdTe solar cell with 1- μm thick absorber: (1) front ($V_{oc} = 676$ mV, $J_{sc} = 19.7$ mA/cm², $FF = 60.5\%$, $\eta = 8\%$) and (2) back ($V_{oc} = 622$ mV, $J_{sc} = 12.2$ mA/cm², $FF = 43\%$, $\eta = 3.2\%$) illuminated ones.

As expected, the short circuit current density is reduced, and the efficiency drops to 7-8% under illumination of the SC from the front side. However, the SC efficiency under the back-side illumination improves up to an exceeding 3% (see Fig. 5). The maximum efficiency is reached after some days under light exposure, and then there is slight degradation, similar to the behavior shown in Fig. 4 for the thicker cell.

7. Conclusion

Application of a novel back contact, based on transparent conductive oxide, on *p*-CdTe opens a variety of new applications of CdTe solar cells. They can work as bifacial cells, illuminating the back and the front surfaces simultaneously or they can be used in tandem solar cells. The controlled insertion of a very limited amount of copper into the ITO back contact permits to have reproducible devices with high efficiencies still keeping the bifacial configuration.

Thin CdTe layer solar cells have been realized with efficiencies exceeding 10%, the reduced thickness of CdTe allows to have a better performance (efficiencies exceeding 3.5%) on the back-side illumination and reduces the amount of CdTe material.

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References

1. M. Houng, F. Jeng, Tunneling effect on the metal-CdTe contact // *Solid State Communs.* **66**(1), p. 1-5 (1988).
2. D.L. Bätzner, A. Romeo, H. Zogg, A.N. Tiwari, Development of efficient and stable back contacts on CdTe/CdS solar cells // *Thin Solid Films*, **387**, p. 151-154 (2001).

3. R.T. Bhaskar, Stability studies of CdTe/CdS thin film solar cells, *Ph.D. Dissertation*, University of South Florida, 2005.
4. R. Mendoza-Pérez, J. Sastre-Hernández, G. Contreras-Puente, O. Vigil-Galán, CdTe solar cell degradation studies with the use of CdS as the window material // *Solar Energy Materials & Solar Cells*, **93**, p. 79-84 (2009).
5. G. Khrypunov, A. Romeo, F. Kurtzesau, D.L. Batzner, H. Zogg and A.N. Tiwari, Recent developments in evaporated CdTe solar cells // *Solar Energy Materials & Solar Cells*, **90**(6), p. 664-677 (2006).
6. J. Zhou, X. Wu, A. Duda, G. Teeter, S.H. Demtsu, The formation of different phases of Cu_xTe and their effects on CdTe/CdS solar cells // *Thin Solid Films*, **515**, p. 7364-7369 (2007).
7. D.L. Batzner, A. Romeo, M. Terheggen, M. Dobeli, H. Zogg and A.N. Tiwari, Stability aspect in CdS/CdTe solar cells // *Thin Solid Films*, **451-452**, p. 536-543 (2004).