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Invited article

Recent developments in evaporated CdTe solar cells

G. Khrypunov[a], A. Romeo[b], F. Kurdesau[c], D.L. Bätzner[d], H. Zogg[e], A.N. Tiwari[e,*,1]

[a]*Kharkov State Polytechnic University, UA-310002 Kharkov, Ukraine*
[b]*Faculty of Science, University of Verona, Ca' Vignal 2, Strada Delle Grazie, 37134 Verona, Italy*
[c]*National Academy of Sciences Belarus, Logoysky Tract 22, Minsk 220090, Belarus*
[d]*The Australian National University, ACTON, ACT 0200, Australia*
[e]*Thin Film Physics Group, Laboratory for Solid State Physics, ETH (Swiss Federal Institute of Technology) Zürich, Technoparkstrasse 1, 8005 Zurich, Switzerland*

Abstract

Recent developments in the technology of high vacuum evaporated CdTe solar cells are reviewed. High-efficiency solar cells of efficiencies up to 12.5% have been developed on soda-lime glass substrates with a low-temperature (<450 °C) process. This simple process is suitable for in-line production of large-area solar modules on glass as well as on flexible polymer films with a roll-to-roll deposition process. Flexible and lightweight CdTe solar cells with a record efficiency of 11.4% have been developed in a superstrate configuration, and 3.5% efficiency mini-modules have been realised in a preliminary development. Deposition of high-temperature stable ITO front contact layer on polyimide is important for high-efficiency cells, as the layer should withstand processing steps maintaining its high electrical conductivity and optical transparency. Another development is an application of a transparent conducting oxide (TCO) ITO as a back electrical contact on CdTe leading to first bifacial CdTe solar cells, which can be illuminated from either or both sides. Accelerated long-term stability tests show that light soaking improves the efficiency of CdTe solar cells with ITO back contacts and performance does not degrade.

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[*] Corresponding author. Tel.: +41 1 4451474; fax: +41 1 4451499.
E-mail address: tiwari@phys.ethz.ch (A.N. Tiwari).

[1] Also at CREST (Centre for Renewable Energy Systems and Technology), Department of Electronic and Electrical Engineering, Loughborough University, Leicestershire, LE11 3TU, UK.

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Stability of CdTe solar cells has been measured after irradiation with high-energy protons and electrons of different fluences. These solar cells exhibit superior radiation tolerance compared to conventional Si and GaAs solar cells for space applications. Because of extreme stability, and high specific power (kW/kg) of flexible solar cells, CdTe has a promising potential for space applications.

Keywords: Solar cells; Thin films; CdTe; Flexible solar cells; Space photovoltaics

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1. Introduction

Polycrystalline CdTe thin film solar cells have shown long-term stable performance [1] and high efficiency up to 16.5% under AM1.5 illumination [2]. Amongst several attractive features, high chemical robustness/stability of CdTe and a simple phase diagram for compound formation are the most important ones for large-area production of solar modules. A distinct advantage of CdTe is the fast deposition by close space sublimation (CSS) process, which allows high throughput and potentially cheap in-line production of solar modules. If produced in large volume, e.g. more than 60 MW/year, their cost could be lower than 1 Euro/Wp and solar electricity generated from such CdTe solar modules would be potentially cheap and cost effective [3].

The often raised concerns on the toxicity of CdTe are perhaps based on a perception of extending the toxicity of "elemental Cd" to a stable "compound CdTe". The facts on the environmental and health (E&H) issues of CdTe based on several extensive investigations, including at the Brookhaven National Laboratory [4] and the National Renewable Research Laboratory, USA [5], prove that CdTe is a stable compound, that E&H issues of CdTe photovoltaics are insignificant, and production of CdTe PV is a better way to contain the risks created by mining of several metals that are routinely used worldwide.

The highest efficiencies in CdTe solar cells have been obtained using a CSS, or other variant deposition process, which requires a high substrate temperature (~550 °C) and special glass substrates. Very high deposition rate is an advantage of the CSS process, but it requires a sophisticated system to control the deposition processes, especially the high temperature of large-area substrates and crucible-evaporators to maintain the required uniformity of layers [6]. Moreover, all the layers deposited prior to the CSS-CdTe deposition have to withstand high temperatures, requiring an excellent stability of the underneath layers and minimal or controlled element diffusion at those temperatures. Therefore, transparent conducting oxide (TCO) front contact and n-CdS layers have to be optimised to withstand such high temperatures (~550 °C) without degrading their electronic and optical properties. Deposition of good-quality CdTe thin layers (~2 μm) for efficient solar cells is another problem in CSS process. Development of flexible CdTe solar cells on polymers is difficult with the CSS process because of the high substrate temperatures encountered during sublimation process.

On the other hand, conventional physical vapour deposition (PVD) process, where CdTe is evaporated in a high vacuum evaporation (HVE) system, has also provided solar cells with efficiencies exceeding 12% on low-cost soda-lime glass substrates [7]. Since CdTe layer in this process is grown at low temperatures ($<400\,^{\circ}$C), most of the TCOs and CdS layers can easily withstand such temperatures without a significant deterioration of their optical and electronic properties. Hence, there is less-stringent requirement on the extreme stability of CdS/TCO layers if solar cells are developed with HVE process. Thermal evaporation techniques for the required temperature regimes are easily scalable and well developed for other applications. For these reasons, HVE process is attractive for a very simple in-line deposition of large-area CdTe solar modules on soda-lime glass substrates, as well as on polymer foils thereby facilitating the roll-to-roll manufacturing of flexible solar modules.

In this paper, we present a review of the recent advances in evaporated CdTe/CdS solar cell technology, including development of bi-facial solar cells on glass and flexible solar cells on polymer films, and their prospects for space applications.

2. Fabrication of solar cells

We have developed a CdTe/CdS solar cell fabrication process in which all the layers are grown by PVD methods [8]. Briefly, commercially available soda-lime glass coated with fluorine-doped tin oxide (FTO) or with in-house sputtered ITO is used as a substrate. CdS layer is grown in a HVE chamber at a substrate temperature of 150 °C and subsequently annealed at 450 °C for recrystallisation, CdTe is then deposited at a substrate temperature of 300 °C in the same chamber without breaking the vacuum. Typical thickness of CdS is 0.1–0.5 μm and CdTe thickness is between 3 and 4 μm. CdTe/CdS junction is activated by evaporating 400–600 nm $CdCl_2$ on to the CdTe surface and subsequently annealing the stack in air at 430 °C for 30 min. Standard back contact consists of an evaporated Cu/Au stack deposited after bromine–methanol treatment of the CdTe surface, followed by a short annealing at 200 °C in air. Solar cells on soda-lime glass substrates developed with this process routinely have a typical efficiency range of 11–12%, while highest efficiencies up to 12.5% have been also obtained [7,8].

3. Development of flexible cells

High-efficiency CdTe solar cells are generally grown in a superstrate configuration where the CdTe/CdS stacks are deposited on TCO-coated glass substrates. The choice of an appropriate substrate is rather crucial for the superstrate configuration; the substrate has to be optically transparent and has to withstand high temperatures during processing steps. Most of the polymer films are not suitable as a substrate for flexible CdTe solar cells except some specific high-temperature stable polyimide films. Generally, these kinds of polyimide have a large optical absorption loss in visible spectral range, but it is possible to minimise the absorption by reducing the polyimide film thickness. Hence, about 10 μm thin polyimide films will have a reasonably high transparency of the flexible substrate [6]. However, these polyimides may not withstand temperatures exceeding 450 °C. We have applied the CdTe/CdS solar cell processing method described in Section 2 to develop flexible solar cells on polyimide films [7].

3.1. Deposition of ITO front contact

TCO deposition is an important issue for flexible CdTe solar cells, since it has to be grown at low temperatures (<400 °C) and the layer should maintain a high conductivity and transparency even after the deposition of CdS/CdTe layers and subsequent $CdCl_2$ annealing treatment in air. Earlier, we tested commercial ITO, SnO_2:F and in-house-deposited ZnO:Al by RF-sputtering as front contact for CdTe solar cells: we could not develop good solar cells on ZnO:Al layers because of unstable optical and electronic properties of those room-temperature-deposited layers [5]. However, recently, high-efficiency CdTe solar cells have been developed on sputtered ZnO:Al layers [9]. High-quality TCO-coated polyimide films are not easily available commercially though such layers have been developed in research laboratories [10]. ITO deposition process was therefore developed in-house on glass and flexible polyimide substrates. The layers were grown in a R.F. magnetron sputtering system and deposition conditions were optimised for thermally stable ITO layers.

We observed that the average transmission of ITO layer in the wavelength range of 400–800 nm can be improved to $T_{400-800} = 88.5\%$ by increasing the O_2 content in the sputtering gas mixture ($Ar + O_2$) up to 3% and by decreasing the R.F. power density to 1500 mW/cm^2. The sheet resistance (R_{Square}) of 0.5 μm thick ITO films, obtained with the above conditions, is 20 Ω/square (Table 1). Decreasing the R.F. power density to 1200 mW/cm^2 caused an increase in the sheet resistance to up to 475 Ω/square without improving the film transparency ($T_{400-800} = 90.5\%$). In order to obtain ITO layers with a low sheet resistance (below 10 Ω/square) and high transparency (above 85%), it was necessary to heat the substrates during ITO deposition. Layers with $R_{\text{Square}} = 9.6\,\Omega$/square and $T_{400-800} = 89.7\%$ were grown at 250 °C substrate temperature while $R_{\text{Square}} = 6.5\,\Omega$/square and $T_{400-800} = 88.6\%$

Table 1
Optical and electrical properties ITO layers on glass substrate before and after annealing at 430 °C for 30 min

Substrate temerature (°C)	Before annealing		After annealing	
	R (Ω/square)	$T_{400-800}$ (%)	R (Ω/square)	$T_{400-800}$ (%)
No heating	20.0	88.5	48.1	89.1
250	9.5	89.7	32.2	90.5
450	6.5	88.6	15.1	89.5

were measured for layers grown at higher temperature of 450 °C. It should be mentioned that these temperatures are indicative values for our system and may not be the actual substrate temperature.

As mentioned earlier, during the successive CdTe/CdS layer deposition at high temperature, a degradation of the ITO properties can take place. It has been observed that $CdCl_2$ annealing treatment, which is essential to attain high efficiencies, influences the physical structure of not only the CdTe layer but also of the layers underneath [13]. Because of this, ITO properties were investigated before and after annealing in air with analogous temperatures as for the $CdCl_2$ treatment (430 °C, 30 min). As shown in Table 1, annealing in air increased the film sheet resistance without a significant change of transmission in the visible region. ITO layers grown at high temperature were considered more suitable for further processing of CdTe solar cells.

The high-temperature sputtering process, described above, was applied to grow ITO layers on commercially available polyimide (Upilex©) films. A pre-deposition annealing treatment of 450 °C for 20 min was applied to clean and stabilise the substrate. The sheet resistance of the ITO layer on Upilex© film was ~5 Ω/square prior to the deposition of CdTe/CdS stack and $CdCl_2$ annealing treatment. The properties of ITO/Upilex© were investigated before and after annealing in air at high temperatures. An annealing of the ITO/Upilex© stack prior to the deposition of CdTe/CdS layers improves the stability of the ITO layer for further high-temperature processes. Annealing in air at 450 °C improves the transmission of ITO/Upilex© from 69% to 72% in the spectral range of 500–900 nm (see Fig. 1), but it also increases the sheet resistance from 5 to 12 Ω/square. Repeated annealing cycles

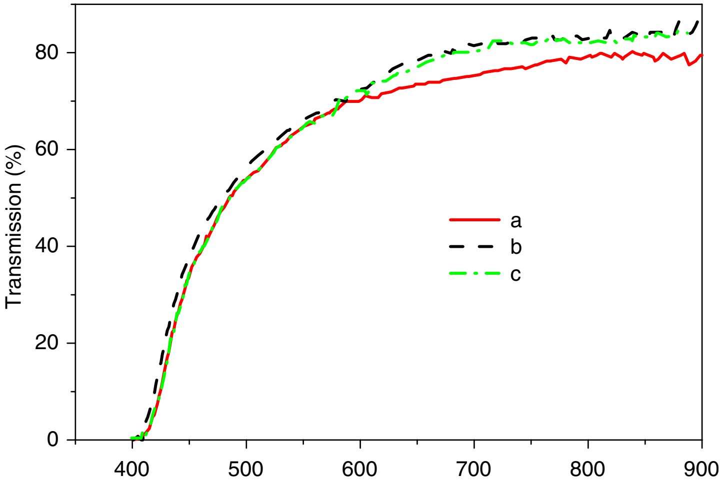

Fig. 1. Optical transmission spectra of a 10 μm thin Upilex© film (a) and ITO/Upilex© structure before (b) and after annealing in air (c).

in the same conditions increase the ITO sheet resistance by only 0.8–0.9 Ω/square, with no degradation in layer transparency.

3.2. Flexible solar cells and mini-modules

The CdTe solar cell fabrication process, described in Section 2, was applied to grow flexible solar cells on differently treated ITO/polyimide films. CdTe/CdS layers were deposited on air-annealed (430 °C, 30 min) and not-annealed ITO/polyimide substrates of $5 \times 5\,\mathrm{cm}^2$ size. After complete processing, solar cells were mechanically scribed to small area ($0.5 \times 0.5\,\mathrm{cm}^2$) for I–V and quantum efficiency measurements.

As shown in Fig. 2, solar cells on a not-annealed ITO/polyimide substrate show an efficiency of 8.5% with $V_{oc} = 746\,\mathrm{mV}$, $J_{sc} = 19.3\,\mathrm{mA/cm}^2$, $\mathrm{FF} = 59\%$. However, solar cells grown on annealed ITO/polyimide yield 11.4% efficiency with $V_{oc} = 765\,\mathrm{mV}$, $J_{sc} = 20.9\,\mathrm{mA/cm}^2$, $\mathrm{FF} = 71\%$ [7]. The higher efficiency of solar cells obtained on annealed ITO films, due to higher values of FF, can be assigned to a higher stability of annealed ITO layers. Solar cells formed on the annealed substrate show also a higher current density despite a slightly higher sheet resistance of the ITO layer.

A comparison of the quantum efficiency measurements (see Fig. 3) of flexible CdTe solar cells on annealed and not-annealed ITO/polyimide substrates shows a higher response (in the spectral region 0.6–0.8 μm) for solar cells on annealed ITO/polyimide film. The overall lower quantum efficiency for both solar cells, compared to a 12.5% efficiency cell on glass, is mainly due to the lower transparency of the polyimide films.

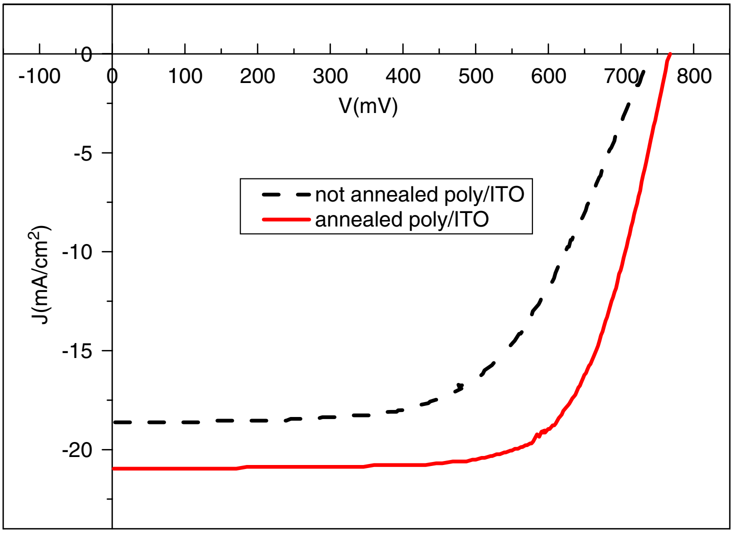

Fig. 2. J–V curves under simulated AM1.5 illumination of flexible CdTe solar cells developed on not-annealed (a) and air-annealed (b) ITO/polyimide films show 8.5% and 11.4% efficiency, respectively.

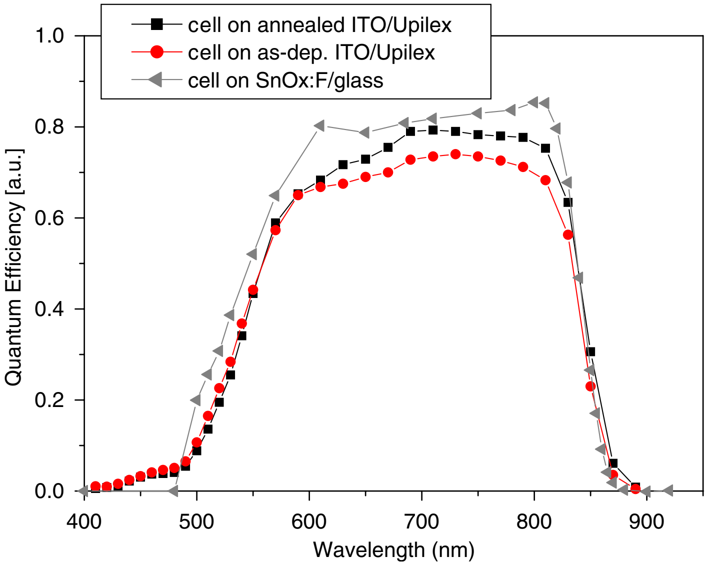

Fig. 3. Comparison of the quantum efficiencies of flexible solar cells on polymide with a 12.5% efficiency cell on glass substrate.

To demonstrate a proof of concept, flexible CdTe mini-modules were developed on $5 \times 5\,\text{cm}^2$ Upilex films using physical shadow masks for isolation and interconnection of solar cells (Fig. 4). Despite several limiting factors contributing to losses, interconnected flexible mini-module of about 3.5% efficiency was developed in the preliminary phase. Higher-efficiency modules can be achieved using more appropriate technologies for scribing and patterning.

The 11.4% efficiency (AM1.5 measurement conditions) flexible solar cell on annealed ITO/Upilex©-polyimide film ($V_{\text{oc}} = 765\,\text{mV}$, $I_{\text{sc}} = 20.9\,\text{mA/cm}^2$, $\text{FF} = 71\%$), shown in Fig. 3, is comparable to the 11% efficiency obtained with in-house polyimide solar cells ($V_{\text{oc}} = 842\,\text{mV}$, $I_{\text{sc}} = 18.5\,\text{mA/cm}^2$, $\text{FF} = 70.9\%$) [8]. It should be mentioned that the properties of the ITO on Upilex© and on in-house developed polyimide may slightly differ since the ITO layers were grown in different sputtering systems under different conditions.

4. Space applications

4.1. Performance stability against proton and electron irradiation

Because of lightweight and high efficiency, flexible CdTe solar cells can yield very high specific power of up to ~2.5 kW/kg (estimated on cell level), while flexibility can lead to easy and low-cost deployable power generating arrays for space applications. Therefore, lightweight and flexible solar modules are not only interesting for

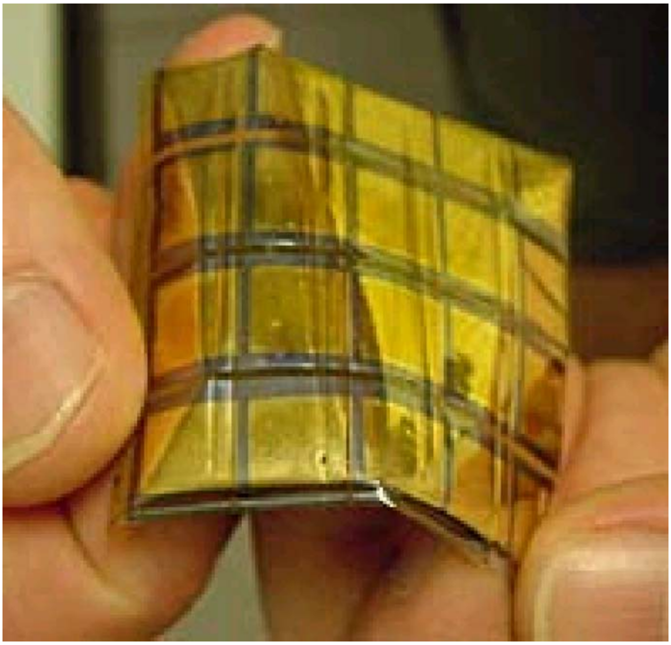

Fig. 4. Flexible CdTe mini-module on a $5\times5\,\mathrm{cm}^2$ Upilex film developed with a shadow mask method.

terrestrial but also for a variety of satellites and space ships provided they can withstand the space conditions. Strong electromagnetic radiation can severely deteriorate the photovoltaic performance of solar cells, as has been widely observed for conventional Si and III–V solar cells. In order to evaluate the potential of CdTe solar cells for space applications, stability of CdTe solar cells developed at ETH Zurich was tested under electron and proton irradiations [11].

CdTe/CdS solar cells, developed on glass substrates, were irradiated with 0.65, 1 and 2.2 MeV protons with fluences ranging from 10^{11} to $10^{14}\,\mathrm{cm}^{-2}$, as well as with high-energy electrons of 1 and 3 MeV with very high fluences between 2×10^{16} and $2\times10^{17}\,\mathrm{cm}^{-2}$. The cells were irradiated, through a very thin back contact, with a perpendicular, monochromatic beam directly incident on the cell layers. The influence of the thin back contact layers on the particle energy is very little, having much less effect than TCO/glass. The details of experimental procedures, measurements, and simulations have been already described [11] but a summary of the results is presented here. Low-energy protons of 650 keV are more damaging than 1 and 2.2 MeV protons; cell efficiencies are not affected for low fluence up to $\sim10^{11}\,\mathrm{cm}^{-2}$; at medium fluence ($\sim10^{12}\,\mathrm{cm}^{-2}$), cell efficiencies slightly increase, especially in case of 1 MeV protons (caused by an increase in V_{OC} of up to 20 mV, irrespective of the proton energy). Only at higher fluence (1–$3\times10^{13}\,\mathrm{cm}^{-2}$), degradation in cell efficiency occurs as the V_{OC} starts to decrease with a strong dependence on proton energy; the current density J_{SC} remains unchanged for fluences of up to $3\times10^{12}\,\mathrm{cm}^{-2}$ but it starts to decrease for cells under higher fluences. For electron-irradiated cells, Voc and FF remain practically unaffected but there is a stronger decrease of J_{SC} compared to proton irradiation case.

4.2. Comparison with other solar cells

It is possible to compare irradiation-induced damage for different cell technologies using the formalism of the displacement damage dose (DD) developed by Summers et al. [12]. The particle fluence can be converted into DD by multiplication with the material-specific NIEL (non-ionising energy loss) parameter. The relative efficiencies of cells, irradiated with all particle energies, can be plotted as a function of DD to represent the degradation characteristic of a solar cell technology. As shown in Fig. 5, CdTe/CdS cells exhibit extreme radiation hardness, superior to all other cell technologies for practical conditions. It appears that at very high dose CdTe seems to degrade more but such irradiation conditions (very high fluences and defect introduction rates) are rarely encountered in space and are considered unrealistic for most of the practical applications, as it would require a lot many years for the collection of such doses. Moreover, measurements have shown that any degradation in cell performance recovers subsequently by itself, they recover very fast when cells are kept at elevated temperature and/or under illumination. Considering that the collection of damaging doses requires several years, the real damage in space would be very low or even not existent because of the self-recovering properties.

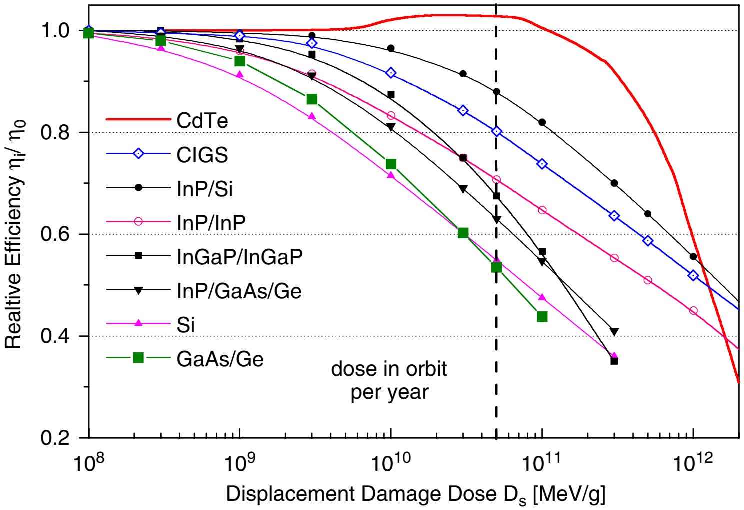

Fig. 5. Comparison of the displacement damage dose vs efficiency characteristics of different solar cell technologies (see Ref. [11] for details) suggests a superior stability of CdTe solar cells under electron and proton irradiation.

5. Bifacial cells

The development of an efficient and long-term stable electrical contact on p-type CdTe is difficult because of both the high electron affinity and high energy band gap of CdTe. The commonly used strategy to develop quasi-ohmic or low-resistance contacts on p-type CdTe has been a chemical etching of the CdTe surface with either a bromine–methanol or a nitric–phosphoric (NPH) acid etch followed by deposition of a very thin buffer layer of metal (Cu, Ni, Sb, etc.) or metal–chalcogenide (Cu_xTe, Sb_2Te_3, ZnTe, HgTe, etc.) and finally a metal layer (Mo, Au, Al, etc.) deposition [13]. Most commonly used Cu-based back contacts yield high-efficiency solar cells but their long-term stability has remained a concern: Cu on one hand dopes CdTe improving the solar cell performance, but on the other hand Cu from the back contact diffuses slowly through the layers degrading the cell efficiency. Avoiding copper in the back contact reduces the efficiency of solar cells.

The best results with "non-Cu containing" contacts are given by Sb_2Te_3/Mo [1,14]. This kind of contact can be deposited either by sputtering or by evaporation technique, and its stoichiometry can be controlled if the substrate temperature is above 200 °C during Sb_2Te_3 deposition. Accelerated stability tests of CdTe solar cells have shown that Sb_2Te_3 provides a superior stability compared to any other back contact [1,13,14]. All these conventional back contacts based on metal/chalcogenide stacks do not allow absorber illumination or spectral transparency through the back contact.

Recently, a new approach has been introduced to apply a transparent back contact on CdTe solar cells: after bromine methanol etching of the CdTe surface, a thin layer of transparent and conducting ITO is sputtered and a short annealing treatment in air is applied at the end [15]. Due to the transparency of the ITO back contact and FTO front contact, solar cell can be illuminated both from the front and rear sides like a bifacial solar cell (Fig. 6).

The *J–V* characteristics (Fig. 7) of a solar cell shows 7.9% efficiency ($V_{oc} = 702\,mV$, $J_{sc} = 18.2\,mA/cm^2$, $FF = 0.62$) when illuminated from the FTO/

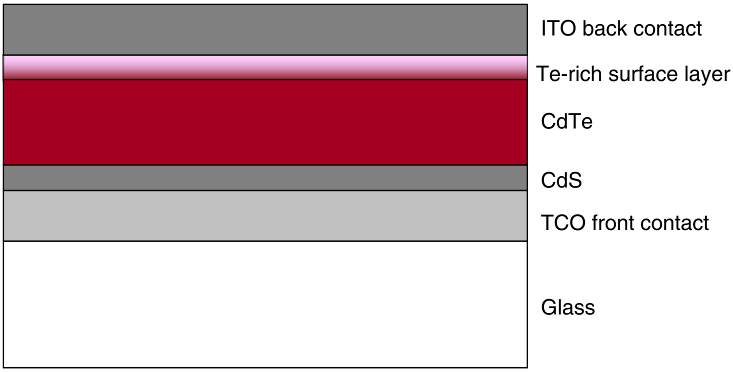

Fig. 6. Schematics of a bifacial CdTe solar cell where TCOs are used as front and back contacts. The solar cell can be illuminated through front and/or back contacts.

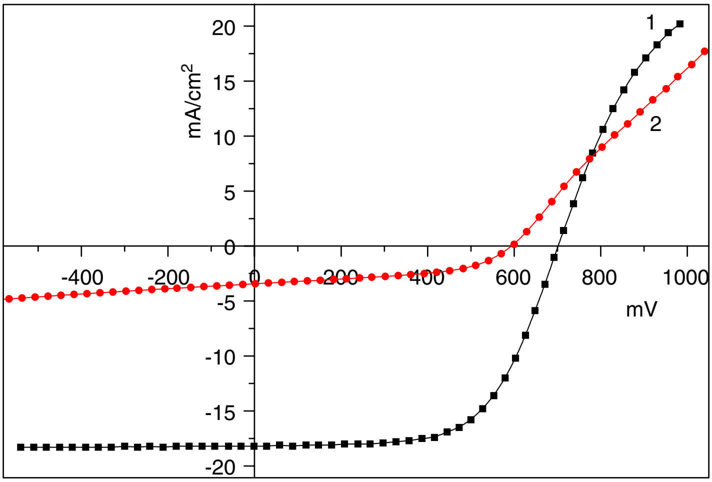

Fig. 7. *J–V* curves measured under simulated AM1.5 illumination for ITO/CdTe/CdS/FTO/glass solar cell illuminated through the front (1) and back (2) contacts.

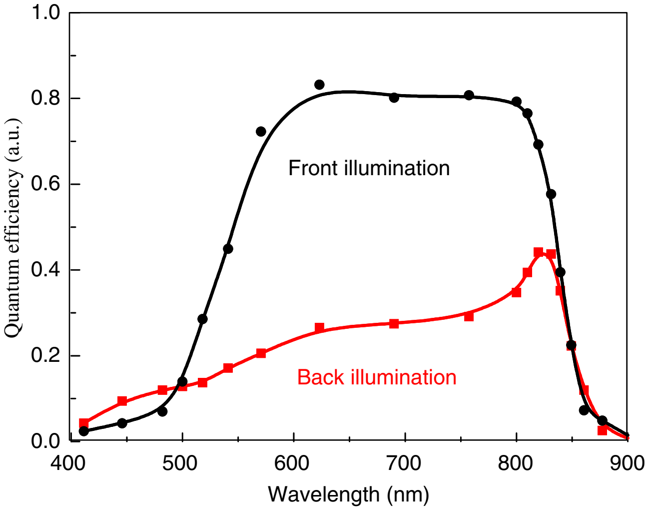

Fig. 8. External quantum efficiency curves of bifacial ITO/CdTe/CdS/FTO/glass solar cell measured by illumination through front and back contacts.

glass side only, and 1% efficiency ($V_{oc} = 591\,mV$, $J_{sc} = 3.4\,mA/cm^2$, FF = 0.5) when illuminated through the ITO back contact only. Quantum efficiency measurements (see Fig. 8) partly explain the reason for low efficiency in back (through ITO) illuminated case: this is because of significantly lower collection of the charge carriers that are photo-generated far away from the CdTe/CdS junction. However, reasons for lower *V*oc and FF need further investigation. CdTe thickness

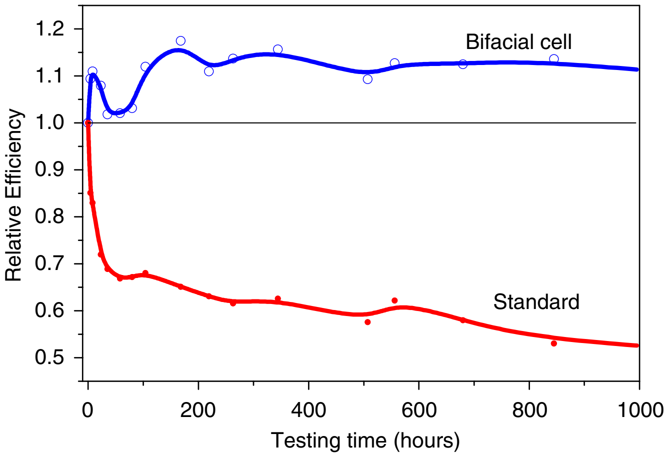

Fig. 9. Accelerated stability tests of evaporated CdTe cells with ITO (bifacial) and Cu/Au (standard) back contacts.

and ITO properties need further optimisation for an optimum performance of the bifacial solar cells.

The most interesting feature of these solar cells is, however, superior stability. The long-term accelerated stability tests of two CdTe cells, one with ITO back contact and another with conventional Cu/Au back contact, are presented in Fig. 9. Solar cells were kept under 1 sun illumination and at 80 °C temperature in open-circuit conditions for these accelerated tests. Cells with ITO back contact show an increase of the performance in the beginning, mostly due to light soaking effect, and a very stable behaviour afterwards, whereas CdTe cells with Cu/Au back contact exhibit a significant degradation in efficiency. As shown in Fig. 10, light soaking improves the *V*oc and FF of solar cells while current remains unaffected.

Such bifacial CdTe solar cells are attractive for tandem solar cells, though band-gap tailoring of the absorber layer would be needed. Moreover, the application of a single compound for front and back contacts with an easily scalable deposition technique such as sputtering (even DC sputtering would be sufficient) makes this configuration very attractive for industrial in-line production, and also suitable for a roll-to-roll manufacturing of solar modules.

6. Conclusions

The development of low-temperature (450 °C) CdTe/CdS evaporation and junction-activation-annealing treatment processes together with the application of thin polyimide film as a substrate allow fabrication of flexible CdTe solar cells in superstrate configuration. For high-efficiency cells, deposition of ITO layer on polyimide and annealing treatments have to be optimised to maintain a high conductivity and transparency of the ITO/polyimide stack. Annealing of ITO/

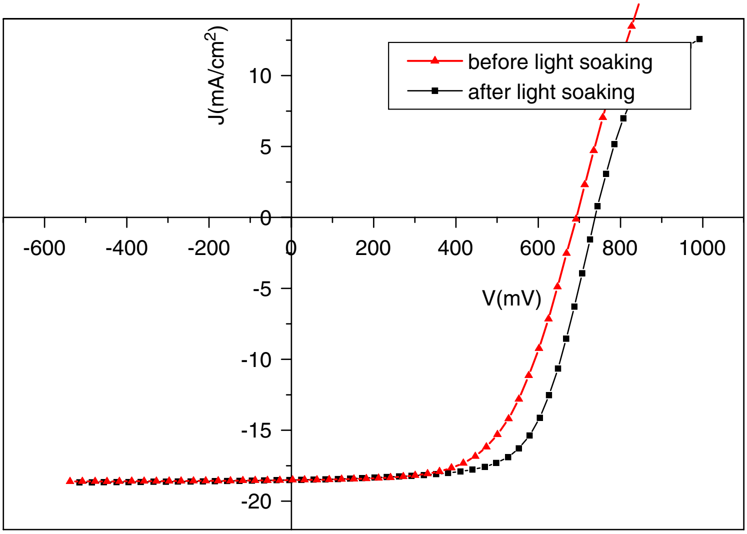

Fig. 10. Light soaking of bifacial solar cell improves the cell efficiency from 7.6% to 9%.

polyimide substrate in air, prior to CdTe/CdS deposition, improves the fill factor up to 71% and J_{sc} up to 20.9 mA/cm^2. Flexible CdTe solar cells with efficiency exceeding 11% and a total thickness of less than 15 μm can deliver very high specific power of ~2.5 kW/kg (estimated on cell level). The deposition processes are suitable for roll-to-roll manufacturing of solar modules.

CdTe thin film solar cells under high-energy electron and proton irradiation show excellent stability; their performance stability under space particle irradiation is superior to those of conventional silicon and GaAs cells. Therefore, CdTe thin film solar cells offer several attractive features for space applications.

Application of a novel back contact, based on TCO, 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. Up to now, 7.9% efficiency (without light soaking) cells have been realised. However, light soaking improves the efficiency significantly; cells with efficiency up to 9% have been measured. Solar cell layers need further optimisation and transport properties need investigation to improve the efficiency of bifacial cells. However, TCO back contact on CdTe provides superior cell stability, simplified processing and a potential for low-cost production.

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