

CdTe Solar Cell in a Novel Configuration

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Polycrystalline thin-film CdTe/CdS solar cells have been developed in a configuration in which a transparent conducting layer of indium tin oxide (ITO) has been used for the first time as a back electrical contact on p-CdTe. Solar cells of 7.9% efficiency were developed on SnO_x:F-coated glass substrates with a low-temperature (<450°C) high-vacuum evaporation method. After the CdCl₂ annealing treatment of the CdTe/CdS stack, a bromine methanol solution was used for etching the CdTe surface prior to the ITO deposition. The unique features of this solar cell with both front and back contacts being transparent and conducting are that the cell can be illuminated from either or both sides simultaneously like a 'bi-facial' cell, and it can be used in tandem solar cells. The solar cells with transparent conducting oxide back contact show long-term stable performance under accelerated test conditions. Copyright © 2004 John Wiley & Sons, Ltd.

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INTRODUCTION

The polycrystalline CdTe/CdS thin-film solar cell is one of the most important photovoltaic devices for cost-effective and clean generation of solar electricity for terrestrial applications.^{1,2} Recent measurements of the photovoltaic performance of CdTe solar cells irradiated with high-energy protons and electrons have proven their excellent radiation tolerance for space applications,³ while it is well known that the performance of conventional Si- or GaAs-based space solar cells severely deteriorates when they are irradiated with high-energy electrons and protons in space. Development of flexible and lightweight CdTe solar cells together with highly stable performance and low production cost make them interesting for low-cost and easily deployable solar power generators in space.

In the most commonly used 'superstrate' configuration for high-efficiency CdTe/CdS solar cells the layers are grown onto the transparent conducting oxide (TCO)-coated glass or polymer substrates, while metal foils or metal coated glass or polymers are used for less efficient 'substrate' configuration solar cells (Figure 1). The CdTe solar cell consists of at least four layers and a similar number of relevant interfaces.

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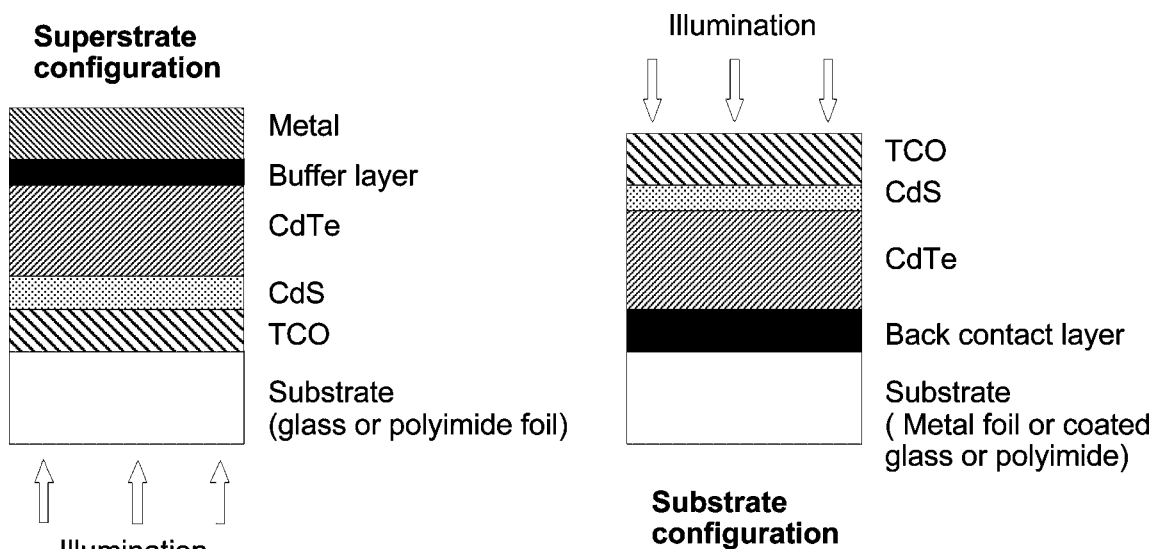


Figure 1. Schematics of the CdTe solar cells in conventional 'superstrate' and 'substrate' configurations

The TCO layer in direct contact with the CdS is called 'front contact', while the metal or metal–chalcogenide layers in direct contact with the CdTe are called 'back contact.' A variety of TCOs, such as fluorine-doped tin oxide ($\text{SnO}_x\text{:F}$), indium–tin oxide (ITO), doped zinc oxide (e.g., ZnO:Al), cadmium stannate (CTO), etc., have been used as a front contact in CdTe solar cells.^{4–6} Numerous papers and reviews have described deposition methods and properties of different TCOs for optoelectronic applications.⁷

The favourable thermophysical properties and chemical robustness of CdTe/CdS facilitate simple and low-cost manufacturing of solar cells with a variety of deposition methods, such as close space sublimation, vapour transport deposition, high vacuum evaporation, sputtering, electro-deposition, spray.^{1,2} The solar cell efficiency depends on the growth process (temperature) and the type of substrate used for deposition. The CdTe layers grown at a high temperature ($\sim 600^\circ\text{C}$) on expensive 'alkali-free' glass yield cells of up to 16.5% efficiency.⁴ While, lower efficiencies of 10–14% are obtained from CdTe layers grown on soda-lime glass by low-temperature (450°C) processes such as sputtering⁸ and high-vacuum evaporation (HVE)^{9–11} methods.

The 'back contact' on CdTe is an important topic of scientific and industrial interest since it influences the efficiency and long-term stability of solar 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 energy bandgap of CdTe. Since metals of high work function (>5.7 eV) are rare, alternative methods are applied to develop quasi-ohmic or low-resistance contacts on *p*-type CdTe. Most commonly used back-contact materials are either metals (Cu/Au, Ni–P, Cu–graphite paste, Sb, etc.) or metal chalcogenides (Cu_xTe , ZnTe, Sb_2Te_3 , HgTe, etc.) that are applied after chemical etching of the CdTe surface with either a bromine–methanol or a nitric–phosphoric (NPH) acid etch.^{9,10} To our knowledge, TCOs have never been used as an ohmic or quasi-ohmic back contact on *p*-CdTe. On the other hand, if the CdTe layer in CdTe/CdS superstrate solar cells contacts the highly conducting TCO front contact, because of pinholes or incomplete coverage by CdS, shunts are caused which reduce V_{oc} and FF, thereby reducing the cell efficiency.¹¹ Therefore, in high-efficiency superstrate solar cells, either a stack of high-resistive TCO/low-resistive TCO is used as a front contact or a thick CdS layer ensuring complete conformal coverage of the conducting TCO is applied for maintaining high V_{oc} and FF.

It is generally accepted that TCOs form a low-resistance ohmic contact with *n*-CdS and *n*-CdTe, while they form a rectifying barrier with *p*-CdTe. There are reports of heterojunction solar cells where TCO is used as a barrier window layer on *p*-type CdTe single crystal, and metals are used as ohmic contact on single-crystal CdTe.^{12–14} In this paper, we describe the development of a CdTe thin-film polycrystalline solar cell in a novel configuration where TCO is used as a back contact on *p*-CdTe instead of any metal or metal chalcogenide layer, and the advantages of this device are discussed.

EXPERIMENTAL RESULTS AND DISCUSSIONS

The materials suitable for a low-resistance ohmic contact or a rectifying barrier on a particular semiconductor are chosen on the basis of the electron affinity rule, taking the bandgap energy and Fermi level into account. But this theoretical criteria quite often does not hold in experimental devices where interface states, charged dipoles, and the existence of an interface buffer layer either through chemical modification or by addition of a thin buffer layer, can strongly modify the band line-up and carrier transport properties across the heterojunction.^{15,16} Development of different ohmic contact processes for *p*-CdTe is a true illustration of the importance of the interface modification.

We have developed CdTe solar cells in a configuration shown in Figure 2. Basically, the structure appears to be a slight modification of the conventional superstrate structure where the conventional back contact has been replaced by a TCO layer. Prior to the TCO deposition the CdTe surface has been modified by a chemical etching and exposure to a plasma containing Ar and O ions. Some of the important features of this novel device are:

1. Unique application of TCO both as a front contact for *n*-CdS and back contact for *p*-CdTe by applying a chemical (etching) and a plasma modification of CdTe for engineering the interface properties.
2. Transparent or semitransparent device, depending on the spectral range and CdTe thickness, that can be used for tandem solar cells, especially for monolithically interconnected ones. However, a higher bandgap (1.6–1.7 eV) absorber layer would be desired for the top solar cell.
3. It can be used as a 'bifacial' solar cell where the device can be illuminated from either or both sides.
4. Potentially superior encapsulation and more stable long-term performance because TCOs are chemically more inert and stable (less diffusive) than most of the metals that have been used in conventional superstrate cells up to now.
5. Highly suitable for industrial manufacturing since the TCO thickness control is not stringent, while a strict thickness control of a few tens of nanometres thin buffer (Cu, HgTe, Sb, Sb₂Te₃, etc.) is very crucial in conventional superstrate cells.

The solar cell presented in Figure 2 can be developed with already known deposition methods and recipes, but the key issues of CdTe surface modification—with chemical and plasma—and subsequent TCO back-contact

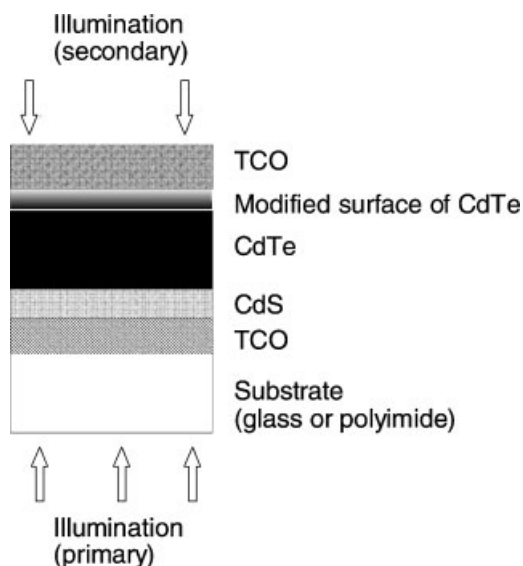


Figure 2. Schematics of the novel CdTe solar cell in which TCO is used for the first time as a back contact on *p*-CdTe. The solar cell can be illuminated from either side. It is a conventional superstrate cell if illuminated only from the substrate side (primary illumination), while it operates like a 'bifacial' cell if simultaneously illuminated from both sides (primary and secondary illumination together). Such a solar cell configuration is also useful for tandem solar cells

deposition require specific optimisations. To prove the viability of this new concept, we have developed solar cells on commercially available $5 \times 5 \text{ cm}^2$ soda-lime glass substrates coated with a $\text{SnO}_x\text{:F}$ (FTO) layer of about $15 \text{ } \Omega/\text{square}$ sheet resistance and about 80% average transmission. A simple vacuum evaporation method was used to grow 500-nm-thick CdS and 4000-nm-thick CdTe layers at 150°C and 300°C , respectively.⁹ For the 'CdCl₂ treatment', about 200-nm-thick CdCl₂ was evaporated on the surface of the CdTe and the samples were subsequently annealed in air at 430°C for 30 min. After that the samples were washed in deionised water and the surface of the CdTe layer was etched in a bromine–methanol solution. Other solutions can also be used, but this process step has not been optimised yet. After etching the samples were immediately transferred into the sputtering system.

The ITO back-contact layer was deposited with a RF magnetron sputtering system (MRC 6031) using a single ITO target. The base pressure in the vacuum system before deposition was 10^{-6} mbar. The ITO deposition was performed at a Ar/O_2 (3 vol% O_2) pressure of 8×10^{-3} mbar and with a RF power density of $1500 \text{ mW}/\text{cm}^2$. The sputtering time was 15 min. Under these conditions ITO films with sheet resistance of about $12 \text{ } \Omega/\text{square}$ and transmission of about 90% are obtained on glass substrates. For optimum properties of the ITO, samples were heated to 250°C prior to the deposition of the ITO layers. After the deposition small area ($3 \times 4 \text{ mm}^2$) solar cells were mechanically scribed and the cell area was accurately measured.

The current–voltage (I – V) characteristics of the solar cells were measured at room temperature under simulated AM1.5 illumination. It was observed that most of the solar cells were in the efficiency range of 7–8%. Figure 3 shows the I – V curve of the highest efficiency solar cell illuminated from the FTO/glass side only, the photovoltaic parameters of this cell are: $V_{\text{oc}} = 702 \text{ mV}$, $J_{\text{sc}} = 18.2 \text{ mA}/\text{cm}^2$, $\text{FF} = 0.62$, $\eta = 7.9\%$. When illuminated only from the ITO back-contact side the typical cell efficiency is about 1%. This is because of significantly lower collection of the charge carriers that are photogenerated far away from the CdTe/CdS junction. The CdTe thickness and properties need optimisation for the back-surface illuminated solar cells.

The average efficiency of reference solar cells with standard Cu/Au back contacts on CdTe is in the range of 10–11%. The slightly lower efficiency of the cells with ITO back contact is because of the lower V_{oc} and

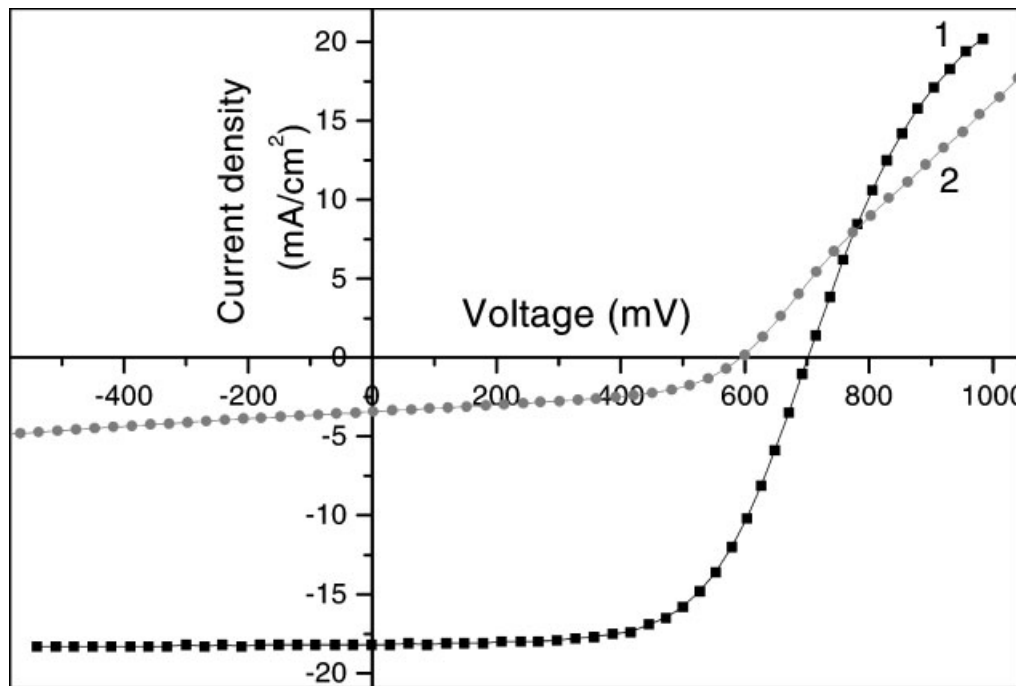


Figure 3. I – V curves of the FTO/CdS/CdTe/ITO solar cell illuminated from: (1) the FTO side ($V_{\text{oc}} = 702 \text{ mV}$, $J_{\text{sc}} = 18.2 \text{ mA}/\text{cm}^2$, $\text{FF} = 0.62$, $\eta = 7.9\%$); and (2) the ITO side ($V_{\text{oc}} = 591 \text{ mV}$, $J_{\text{sc}} = 3.4 \text{ mA}/\text{cm}^2$, $\text{FF} = 0.50$, $\eta = 1.0\%$) under simulated AM1.5 illumination

FF values. They are due to the high series resistance of the cells. Optimisation of the ITO deposition for lower resistance is certainly necessary, but application of a metal layer or a grid on ITO will increase the FF and V_{oc} , and thereby the efficiency of solar cells. Further, a reflective metal layer on the ITO (or other TCO) back contact will enhance the current also, and help in reducing the absorber layer thickness. Apart from these, an optimisation of the CdTe surface with chemical etching and plasma modification is fundamentally important for further improvement in cell efficiency.

A detailed chemical and electronic characterisation of the CdTe–TCO interface region is essential to explain the current transport at the back contact. Tunneling is a probable mechanism, but measurements are needed to ascertain it. In fact, the formation of ohmic contacts by tunnelling between p^+ and n^+ semiconductors is well known in III–V multi-junction solar cells. Recently, replacement of the classical metal (Mo) contact with the TCO contact has also been demonstrated for I–III–VI₂ thin-film solar cells.^{17,18}

In our earlier work¹⁰ on the development of back contacts on the close space sublimation (CSS) grown CdTe (supplied by ANTEC Solar GmbH) cells, we observed that etching with NPH (a diluted mixture of nitric and phosphoric acids) produced a crystalline and conducting Te surface layer, while an evaporated Te layer was more resistive. In that case the etched Te layer reduced the barrier height at the back contact and facilitated a thin tunnel junction. The diluted bromine–methanol solution used in the present work is a relatively milder etch, which is known to clean the oxide residues on the surface of the CdCl₂ treated CdTe and produce a thin surface layer of Te. The thickness of this surface layer is not determined and also the chemical state is not known.

Preliminary tests of the long-term stability of the solar cells were performed by continuous illumination of the non-encapsulated cells kept in open-circuit conditions under approximated 1 sun AM1.5 conditions. The temperature inside the illumination chamber was maintained at 80°C. The solar cells with TCO back contact did not degrade, rather their performance slightly improved upon light soaking.¹⁹ In contrast, the efficiency of the reference solar cells with standard Cu/Au contact decreased by more than 30% of the initial value.

CONCLUSIONS

A novel configuration for the CdTe/CdS solar cell is introduced in which a TCO layer is used as a back contact on the p -CdTe layer. This solar cell opens a variety of possibilities for applications as it can be illuminated both from the front and back surface simultaneously, thus operating like a ‘bi facial’ cell. Additionally, these solar cells can be used in tandem solar cells since both the contacts are transparent and conducting. However, efficient tandem solar cells will require a thinner and higher bandgap II–VI absorber layer in the top cell.

Single-junction CdTe/CdS solar cells are obviously interesting for terrestrial and space applications. Such solar cells with TCO contacts are expected to be more stable than conventional cells with metallic back contacts, because of their chemical robustness and compatibility. Although, preliminary measurements support this hypothesis, more long-term stability tests are needed. Using a low-temperature process, which is suitable for the development of flexible cells on polyimide, we have demonstrated the concept by developing 7.9% efficient cells on glass substrates using FTO as a front contact for CdS and ITO as a back contact on CdTe. The key steps of the CdTe surface modification and the ITO deposition need further optimisation for efficiency improvement, and investigation of the electronic interface properties is needed to understand the current transport mechanism.

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