



A highly efficient and stable CdTe/CdS thin film solar cell

N. Romeo, A. Bosio, R. Tedeschi*, A. Romeo, V. Canevari

*Dipartimento di Fisica, INFN – Istituto Nazionale di Fisica della Materia, Università di Parma,
Viale delle Scienze, I-43100 Parma, Italy*

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Abstract

In this paper we describe the fabrication and characteristics of highly efficient and stable CdTe/CdS thin film solar cells. Our cells are prepared in three subsequent phases. Firstly, we deposit via sputtering, without solution of continuity a layer of CdS on top of the front contact made up of a double layer of ITO/SnO₂ deposited on a soda lime glass substrate. The second phase consists in the treatment of the CdS layer, which is the key factor for the fabrication of a good heterojunction, with CdCl₂ and in the subsequent deposition of the CdTe layer via close space sublimation technique. Finally, the back contact is fabricated via sputtering making use of the Sb₂Te₃ compound which guarantees the cell stability. Under global AM1.5 conditions the open-circuit voltage, short-circuit current and fill factor of our best cell, fabricated without antireflecting coating and normalized to the area of 1 cm², were $V_{oc} = 858$ mV, $J_{sc} = 23$ mA/cm² and $ff = 74\%$, respectively, corresponding to a total area conversion efficiency of $\eta = 14.6\%$. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Thin film solar cell; Fill factor; Atomic force microscopy

1. Introduction

Since the realization of the first thin film solar cell based on CdTe [1] and from the work of Bonnet, who in 1970 showed the actual possibility of realising a thin film solar cell based on CdTe/CdS heterojunction [2], the performance of this kind of device has

* Corresponding author.

greatly improved. In particular the efficiency has, since then, steadily improved overcoming the threshold of 10% in 1982 [3]. Nowadays the efficiency is well over 15% [4–6]. Despite these remarkable results the preparation of thin film solar cells based on the CdTe/CdS heterojunction still exhibits quite a few open problems and is therefore subject to a noteworthy margin of progress. It is common knowledge that the role of CdCl₂, though fundamental for the good performance of the device, is far from being fully clarified [7,8] as is the open question of the formation of deep level traps in the CdTe layer [9]. Another question which is still open and deserves careful attention 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, use is made of various metals like Cu, Hg, Pb or Au [10–14] which, due to their ability of diffusing in the different layers may deteriorate the device.

In this paper, the method and the materials used to fabricate a highly efficient and stable thin film solar cell based on CdTe/CdS heterojunction are described. In particular, in order to realize a device easily scalable for industrial needs, we paid careful attention both to the process and to the final cost of the device. Despite these narrow constraints we have been able to fabricate thin film solar cells, without antireflecting coating and with surfaces ranging from 0.5 to 0.8 cm², with a high degree of reproducibility proved by an efficiency and a fill factor consistently around $\eta = 14.5\%$ and $ff = 0.74$. We ascribe these good results to the special care we devoted to the treatment both of the CdS layer and the CdTe layer via the CdCl₂ and to our back contact fabricated with the Sb₂Te₃ compound which assured remarkable cell stability.

2. Experimental procedure

A prototype of the solar cell studied in this paper is depicted in Fig. 1.

2.1. The substrate preparation

The substrate used for the deposition was a 1 in² soda lime glass previously washed with a low alkaline detergent and then carefully rinsed in deionized water. Finally, the substrate was rinsed again with acetone and with iso-propyl alcohol (Propan-2-ol) in an ultrasonic bath.

2.2. The front contact

Due to its low-cost soda lime glass is suitable for industrial production [15]. However this undeniable benefit is partially reduced because the sodium contained in this type of glass diffuses, during thermal treatments, into layers which constitute the solar cell. To avoid this problem, a passivating SnO₂ layer is often deposited on the substrate [5,16]. We adopted a new scheme, which consists initially in the deposition via magnetron RF sputtering of 1 μm of ITO under an argon pressure of 1×10^{-2} mbar and at the temperature of 400°C with a deposition rate of 6 Å/s. This

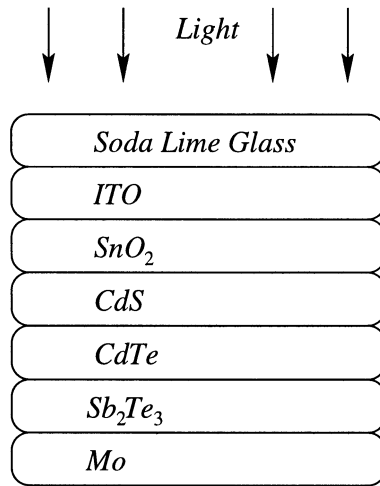


Fig. 1. CdS/CdTe thin film solar cell structure.

first deposition results in an ITO layer with a sheet resistance of $R_s = 1 \Omega \square^{-1}$ which still allows the diffusion of sodium as is evident by the appearance of dendritic crystals of NaCl when the surface of this layer is treated with $CdCl_2$. On top of this first layer we deposited $0.5 \mu m$ of SnO_2 with an O_2 partial pressure of 2×10^{-4} mbar keeping all the other parameters constant. Under these sputtering conditions SnO_2 grows in a very compact polycrystalline structure with a sheet resistance $R_s = 10 \Omega \square^{-1}$. This second layer, despite its greater resistance, does not modify the overall resistance which keeps its minimum value with the great advantage of stopping the sodium diffusion.

2.3. The CdS layer

The good quality of a thin film solar cell is strongly dependent on the proper interaction among the different layers which constitute the device. We therefore deposited, still via magnetron RF sputtering, without removing the sample from the apparatus, a 2000 \AA thick layer of CdS under the following conditions: $T_s = 200^\circ C$, $D = 3 \text{ \AA/s}$, $P = 1 \times 10^{-2}$ mbar, where T_s is the substrate temperature, D the deposition rate and P the argon pressure. On top of the CdS layer a 1500 \AA thick layer of $CdCl_2$ is then evaporated. Subsequently the whole system:

Glass/ITO/ SnO_2 /CdS/ $CdCl_2$

is annealed in air in a two-step process, the first at $460^\circ C$ and the second at $500^\circ C$, both steps for a duration of 20 min. The system is then washed in methanol to get rid of the residual traces of $CdCl_2$.

The beneficial effects of the $CdCl_2$ treatment of the CdS layer have been ascertained carrying out a thorough analysis of the morphology, grain size, ordering and optical

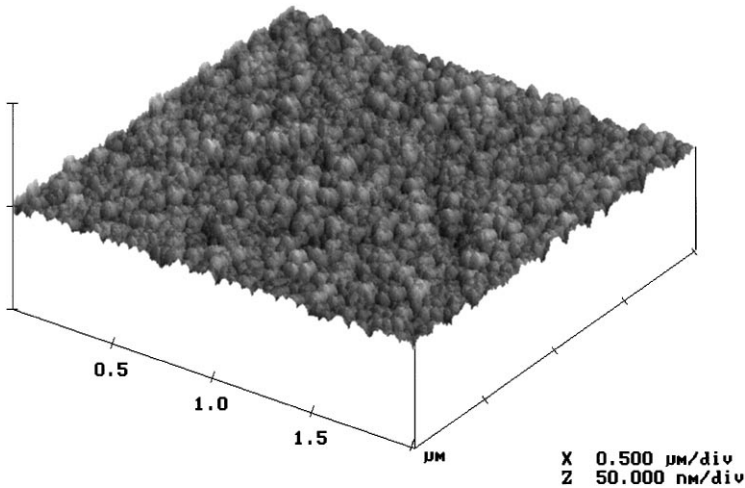


Fig. 2. AFM picture of the CdS layer before CdCl₂ treatment.

properties of the polycrystalline CdS layer prior and after the CdCl₂ treatment. To carry out our investigation we made use of atomic force microscopy (AFM, Digital Instruments Nanoscope IIIA), X-ray analysis (Siemens diffractometer D500 working in the Cu K_α radiation region 1.54060 Å) and transmission spectra (Varian 2390 Spectrophotometer). The results of the AFM analysis, depicted in Figs. 2 and 3, have shown that the CdS morphology and compactness remain good both before and after the treatment. In particular, a fast Fourier transform analysis has indicated that the average lateral size of the crystallites has changed from 500 Å, before the treatment, to 2000 Å, after the treatment.

X-ray analysis carried out before and after the treatment confirmed the AFM results and showed the presence, before the treatment, of a single line at 26.65°, depicted in Fig. 4, which can be attributed to the [0 0 2] hexagonal phase as well as to the [1 1 1] cubic phase. On the contrary, after treatment, the hexagonal phase is more evident since, as is shown in Fig. 5, the [1 0 3] line clearly appears while the [0 0 2] line is narrowed indicating a better overall morphology. Finally, the transmission spectrum reported in Fig. 6 gave an additional confirmation of the beneficial effects of the CdCl₂ treatment from the point of view of the CdS optical properties.

2.4. The CdTe layer

The CdTe is deposited via close-spaced sublimation (CSS) technique on the Glass/ITO/SnO₂/CdS

system previously treated in the CSS chamber with H₂ at 350°C to clean out the non stoichiometric presence of sulfur and any remaining traces of CdCl₂. The actual CdTe deposition is then carried out putting in a graphite crucible a CdTe target normally

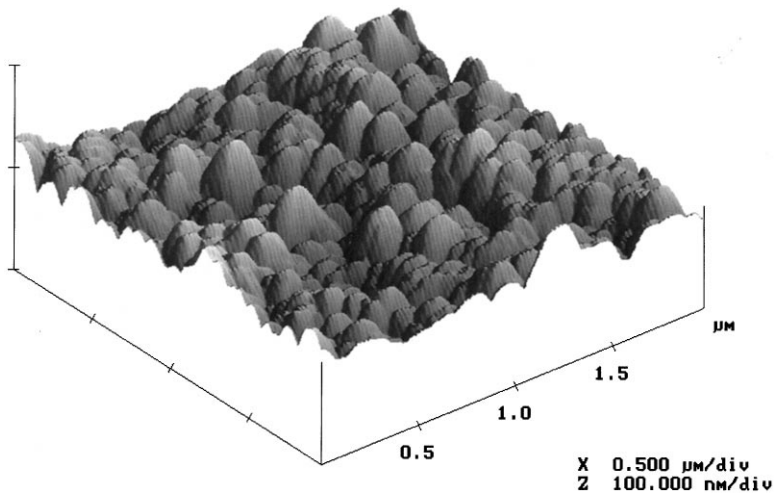


Fig. 3. AFM picture of the CdS layer after CdCl₂ treatment.

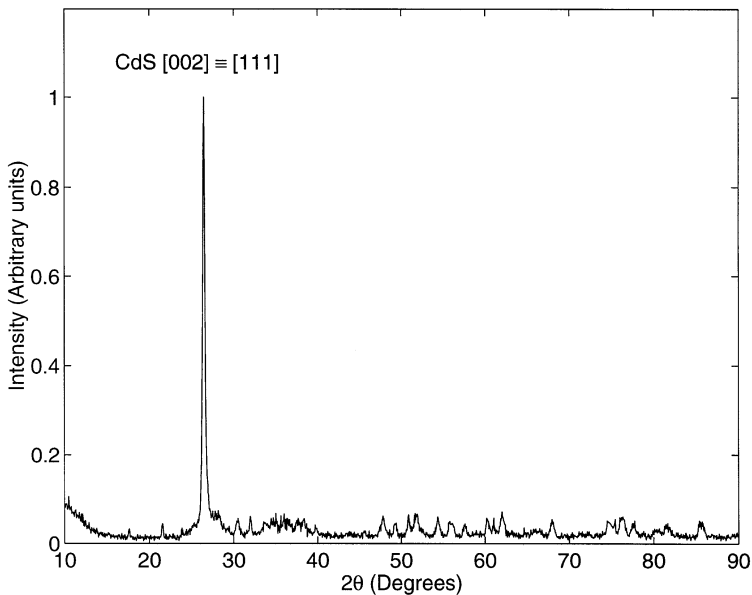


Fig. 4. X-ray spectrum of the CdS layer before the CdCl₂ treatment. In the present and following picture, to make the spectrum more legible, we eliminated the peaks belonging to the ITO/SnO₂ layer.

used for the RF sputtering technique. The target, supplied by CERAC with 6 N purity is disc shaped with a 3.0 in diameter which ensures a very uniform deposition because of its wider dimension with respect to the substrate. The deposition parameters were: $d = 2\text{--}4$ mm, $P = 1$ mbar, $T_c = 610^\circ\text{C}$ and $T_s = 500^\circ\text{C}$ where d is the distance

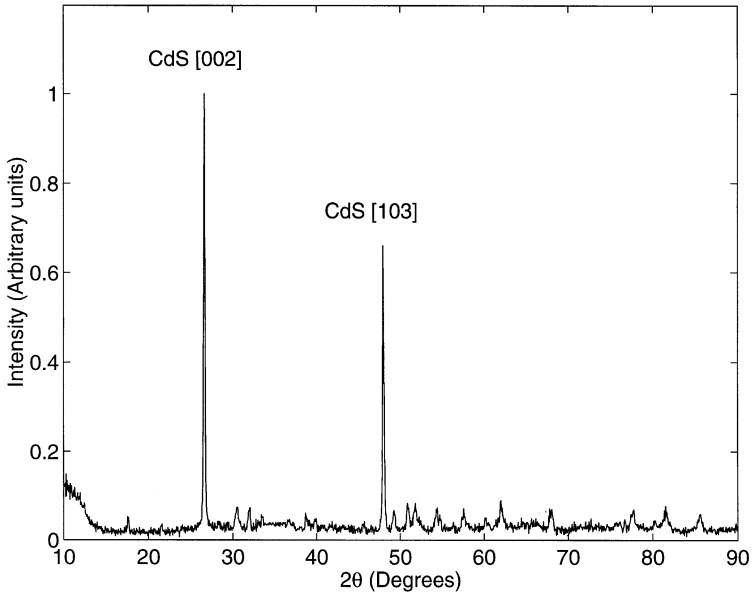


Fig. 5. X-ray spectrum of the CdS layer after the CdCl₂ treatment.

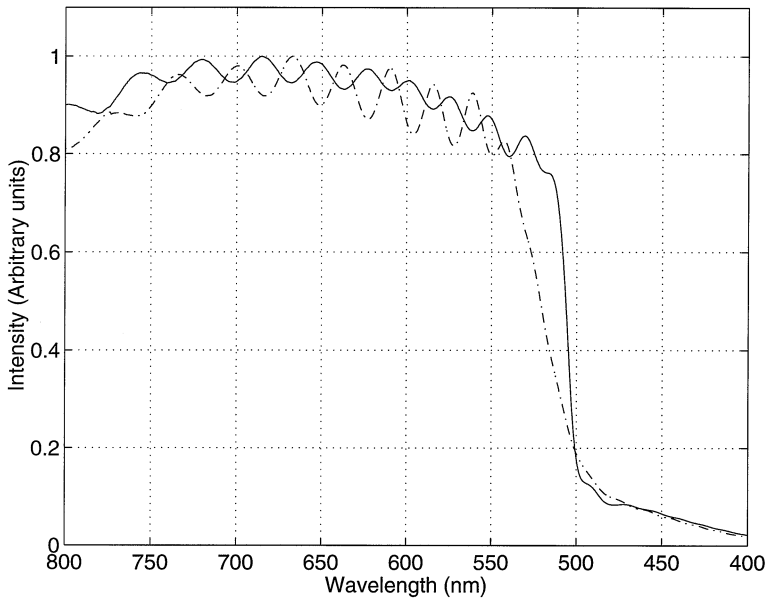


Fig. 6. Transmission spectrum of the CdS layer, before the CdCl₂ treatment (dash-dotted line) and after the treatment (solid line). The shift towards the right of the absorption edge proves the beneficial effect of the CdCl₂ treatment.

between the CdTe target and the CdS surface, P the argon pressure, T_c the crucible temperature and T_s the substrate temperature. Under these conditions a 6 μm thick layer of CdTe is typically deposited in a time span of 5 min.

The beneficial effects of the CdCl_2 treatment of the CdS/CdTe heterojunction are well known in terms of grain growth, reduced interface recombination, increased carrier collection and reduced number of defect states at or near the CdS/CdTe interface. Yet it has to be recalled that the CdCl_2 treatment generates cadmium vacancy-halogen complexes such as $(V_{\text{Cd}}\text{Cl})^-$ which behave as acceptor like traps in the range 0.54–0.9 eV above the valence band edge. These deep traps, though important for the diode current transport, unfortunately have a nonhomogeneous distribution inside the CdTe layer, which results in a detrimental effect on the open-circuit voltage [17,18]. In order to control the formation of these deep level traps as much as possible and to improve the cell performance still making use of the CdCl_2 treatment, we compared the efficiencies of quite a few cells treated with different thicknesses of CdCl_2 deposited by evaporation and then annealed in dry air at different temperatures. The best results were shown by cells treated with a thickness of 3000 Å of CdCl_2 and annealed for 30 min at temperatures around 430°C.

2.5. The back contact

Contacts for thin film solar cells have always been a crucial problem because the presence of metals used for their fabrication limits the lifetime of the device. We attacked the problem covering the CdTe surface, previously etched with $\text{Br} : \text{CH}_3\text{OH}$, with a 100 nm layer of Sb_2Te_3 deposited via RF magnetron sputtering and followed by a final 100 nm thick Mo layer still deposited in the same sputtering chamber. Sb_2Te_3 is a p-type compound which exhibits a low gap (of the order of 0.3 eV) and a resistivity as low as $10^{-4} \Omega \text{ cm}$. Being a stable compound Sb_2Te_3 should not give way to element diffusion in the CdTe matrix.

3. Results

It is our opinion that the results here reported are the consequence of two important factors which are the role of the CdCl_2 in the fabrication of the CdS layer and the Sb_2Te_3 backcontact. We will discuss here these two topics closing with the characteristics of one of our best thin film solar cells.

In principle, one cannot fabricate a good CdS/CdTe heterojunction because of the great lattice mismatch between the two crystals. However, the high miscibility of the CdTe with the CdS at temperatures around 500°C favors the formation of a heterojunction with few interface states. This is due to the presence of a smooth transition $\text{CdS} \rightarrow \text{CdTe}$ through a mixed compound $\text{CdS}_{1-x}\text{Te}_x$ with x varying between 0 and 1. Unfortunately, this type of heterojunctions possesses limited efficiency because the transition $\text{CdS} \rightarrow \text{CdTe}$ occurs through too many atomic layers which inevitably affect the open-circuit voltage and consequently the fill factor. Nevertheless, the high miscibility of the CdS and CdTe can be exploited provided that a proper CdS layer is

Table 1
Comparison between an untreated CdS cell and our best cell

	V_{oc} (mV)	J_{sc} (mA/cm ²)	Fill factor (%)	Efficiency (%)
Untreat CdS	750	22	0.62	10.2
Treated CdS	858	23	0.74	14.6

fabricated. It is here that the role of CdCl₂ treatment of the CdS shows its importance. In fact if the CdTe grows on the surface of an untreated CdS surface the result is again a bad junction, because the CdS crystallites being very small expose a large surface to the CdTe attack, thus allowing a slow transition CdS → CdTe. On the other hand, if the CdTe grows on the surface of a CdS layer previously treated with CdCl₂, then the good morphology and compactness of the polycrystalline film does not allow marked mixing therefore favoring the formation of a junction which develops in a few atomic layers still carrying a small amount of interface states. We experimentally verified this behavior, as is shown in Table 1, through a remarkable increase in the open-circuit voltage and consequently in the fill factor which was consistently over 72% for all the thin film solar cells built up with the CdS layer treated with CdCl₂.

The quality and validity of the Sb₂Te₃ back contact has been investigated by studying the behavior of the cell J vs. V characteristics during a period of six months keeping the cell at room temperature and under open-circuit conditions. At the end of this period, since the parameters of the cell did not show any appreciable variation, we tested the cell under the illumination of ten suns and at the temperature of 60°C. Under these more demanding conditions we did not notice any appreciable degradation of the cell performance apart from a slight increase of V_{oc} (10–30 mV) while the fill factor suffered a decrease which after repeated checks was never greater than 1%.

At present we do not possess data concerning the backcontact series resistance of the CdTe because the sheet resistance of CdTe films is too high to allow a measurement of the contact series resistance using, for example, the four probes method. To shed some light on this issue we are actually planning, in the near future, to carry out such a measurement on a low-resistivity ($< 1 \Omega \text{ cm}$) p-type CdTe single crystal. As a final remark on the Sb₂Te₃ backcontact we are aware that the sputtering deposition technique might be an important factor with respect to the good performance of the cell. A reasonable answer to this point can be found by noticing that, since Sb₂Te₃ is deposited on a substrate kept at a temperature of 300°C, some Sb could slightly diffuse into the CdTe matrix making a thin p⁺ CdTe layer in contact with the low resistivity Sb₂Te₃ film thus facilitating the formation of an ohmic contact. Anyhow, to unravel the question of whether high-energy ions might be the important factor for the ohmic contact, Sb₂Te₃ will be soon deposited on CdTe by evaporation.

The J vs. V characteristics of one of our best CdS/CdTe solar cells are shown in Fig. 7. The cell was fabricated without antireflecting coating with an area of 0.64 cm² and its characteristics were measured in the dark and under illumination. The characteristics of the cell, measured under the typical conditions of 300 K,

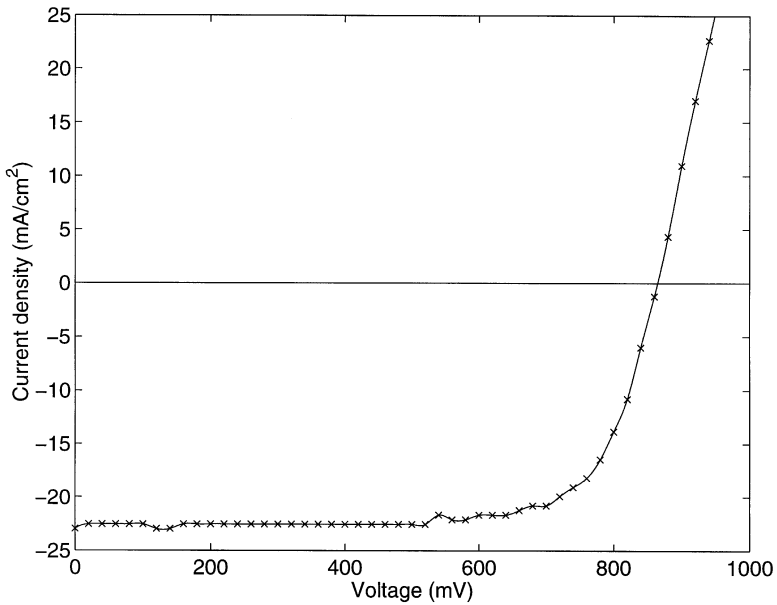


Fig. 7. *I*–*V* characteristic of our best cell fabricated without antireflecting coating (area = 0.64 cm², temp = 300 K, irradiance = 100 mW/cm², AM = 1.5, *V*_{oc} = 858 mV, *J*_{sc} = 23 mA/cm² and ff = 74% corresponding to a total area conversion efficiency of $\eta = 14.6\%$).

Table 2
Cell performance

	Best cell ^a	Our best cell ^b
<i>J</i> ₀ (A/cm ²)	2–5 × 10 ⁻¹²	1.1 × 10 ⁻¹¹
Diode factor <i>A</i>	1.6–1.9	1.75
<i>J</i> _{sc} (mA/cm ²)	25.1	23.0
<i>V</i> _{oc} (mV)	843	858
Fill factor (%)	74.5	74.0
Efficiency (%)	15.8	14.6

^aThese data have been taken from the paper of J. Britt et al. [5].

^bValues without antireflecting coating and normalized to the cell surface of 1 cm².

100 mW/cm² and AM1.5 making use of a solar simulator supplied by ORIEL were *V*_{oc} = 858 mV and *J*_{sc} = 23 mA/cm² with a fill factor of 74% corresponding to a total area conversion efficiency of 14.6%. The dark *J* vs. *V* characteristics yielded a diode quality factor *A* = 1.75 which was evaluated assuming the standard formula

$$J = J_0(e^{qV/AkT} - 1), \tag{1}$$

where *J*₀ is the dark saturation current, *V* the bias potential, *q* the electron charge, *k* the Boltzmann constant and *T* the temperature. Our diode quality factor is close to

the value reported by Britt and Ferekides [5]. According to the theory a diode factor of 1.75 is indicative of recombination within the junction [19,20] and it does not exclude the possibility of an embedded homojunction in the CdTe layer.

To conclude the present paper we show, in Table 2, a comparison between our data, normalized to an area of 1.0 cm², and the data of the best cell known so far, to give an idea of the performance of our cell.

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