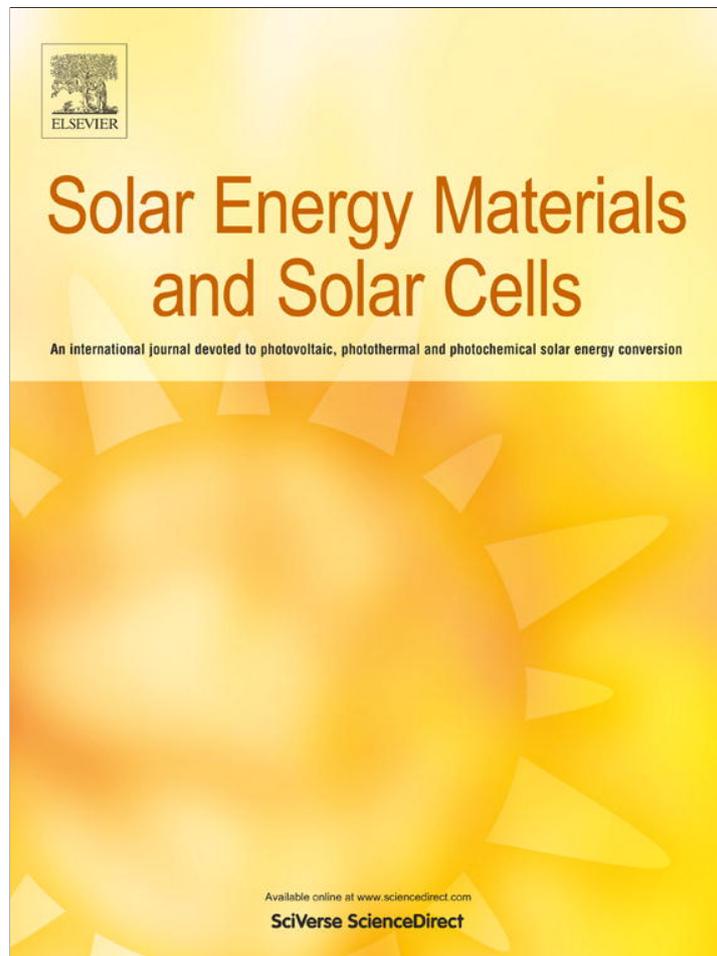


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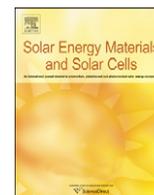
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Study of difluorochloromethane activation treatment on low substrate temperature deposited CdTe solar cells

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ABSTRACT

In this paper we describe a low substrate temperature CdTe fabrication process by vacuum evaporation (VE) where the recrystallization step avoids the use of CdCl₂, which is a carcinogenic material. In our process CdS and CdTe are deposited at pressures of 10⁻⁶ mbar in the same chamber by thermal evaporation and with substrate temperature of 150 °C and 340 °C, respectively. The CdTe/CdS/TCO stacks are then put in a quartz chamber and, after having previously pumped the chamber down to 10⁻⁵ mbar, a controlled mixture of argon and chlorine containing gas is fluxed with a substrate temperature in a range between 400 °C and 450 °C. The morphological properties of the single layers are studied by X-ray diffraction (XRD), atomic force microscopy (AFM), cathodo-luminescence (CL) and the electrical properties of the finished devices are presented by means of current–voltage (*I*–*V*) and capacitance–voltage (*C*–*V*) measurements.

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1. Introduction

CdTe photovoltaic technology has finally reached the technological maturity and is now one of the best selling type of product among thin film solar cells. High efficiency and low cost panels are routinely produced on glass substrates by different companies in the world.

CdTe solar cells are typically grown on soda lime or alkali free glass at temperatures between 400 °C and 550 °C and they can be grown in substrate or superstrate configuration.

In the most common superstrate configuration transparent conductive oxide (TCO), such as indium tin oxide (ITO), tin oxide doped with fluorine (FTO) or zinc oxide doped with aluminum (ZAO), is typically deposited on glass followed by CdS and CdTe deposition. After the CdTe recrystallization treatment, a metal back contact is deposited and the finished device is illuminated from the substrate side [1].

The goal of this work is to analyze an alternative method of CdTe activation (namely “Freon[®] treatment”: by applying difluorochloromethane gas at high temperature) introduced successfully for close space sublimated (high substrate temperature) CdTe by Romeo et al. [2], on low substrate temperature grown CdTe in order to investigate the re-crystallization mechanisms and to compare them with the standard CdCl₂ treatment [1] for low

temperature deposited devices by vacuum evaporation (VE). As a matter of fact, for low temperature material the polycrystals have a strong rearrangement of the grains with a clear enlargement of their size, while generally for CSS deposited samples this is not the case [1].

Freon[®] R-22 is a greenhouse gas and from 31st December 2009 it is available only as recycled gas. In this work we wanted to compare previous work on CSS made CdTe with evaporated ones, for this reason R-22 has been taken into account; however, alternative chlorine containing gases can also be used.

CdTe solar cells were grown in superstrate configuration. Two different treatments – CdCl₂ treatment in methanol solution or Freon[®] treatment in vacuum – were used to activate the cell. Back contact was made by evaporation of Cu and Au in vacuum. The morphological properties of the single layers were studied by atomic force microscopy (AFM), the structural properties of CdTe films treated with Freon[®] and CdCl₂ were studied by X-ray diffraction (XRD) and cathodo-luminescence (CL), finally the junction and device properties were analyzed by current–voltage (*I*–*V*) and capacitance–voltage (*C*/*V*) techniques.

2. Materials and methods: Solar cell fabrication

In our labs solar cells are fabricated by depositing each single layer (except for the front contact), namely CdS, CdTe and back contact, by vacuum evaporation.

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2.1. Front contact deposition

For TCO two different glass coatings have been used: a commercially available ITO film coated glass with a SiO₂ barrier layer and a laboratory scale bi-layer of conductive ITO+thin insulating ZnO, deposited at high temperature.

The first one is a commercially prepared ITO with a thickness of 180 nm and a sheet resistance of 10 Ω/square.

The second one is a 400 nm ITO+100 nm intrinsic ZnO deposited by radio frequency-sputtering at a temperature of 400 °C with a sheet resistance below 5 Ω/square, due to its high substrate deposition temperature this layer is much more crystallized and stable; moreover because of the ZnO layer, which acts as a barrier to diffusion of impurities, indium diffusion is avoided. A comparison of the devices made on these two different substrates will outline some of the properties observed.

2.2. Window layer fabrication

CdS is evaporated in vacuum at a pressure of 10⁻⁶ mbar using direct current heating of a molybdenum crucible and deposited on the glass/TCO stacks at a substrate temperature of 150 °C with a deposition rate ranging from 0.15 nm/sec to 0.45 nm/sec (controlled by a quartz crystal thickness monitor). After deposition, CdS was annealed by heating the stacks in vacuum for 30 min (in order to increase the stability of CdS to the subsequent depositions and CdTe activation treatment), a slight re-crystallization of the grains was observed by AFM with an enlargement of the grain size from 50–100 nm to 100–200 nm, not shown here.

2.3. CdTe deposition and post-deposition treatment

After deposition and treatment of the CdS layer, CdTe is deposited in the same chamber by heating a special in-house made graphite crucible at a substrate temperature ranging from 300 °C up to 340 °C and deposition rate of about 2 nm/s.

A typical CdTe layer for our devices is 3.5/4 μm thick with quite compact morphology and grain size of about 1 μm as shown in Fig. 1; the morphology and the grain size is depending not only on the substrate temperature but also on the TCO. CdTe deposited on commercial ITO and ITO+ZnO shows a similar but not same morphology, grain size is typically around 1 μm for both but it results to be much more compact in the second case. Compared to the close space sublimated (CSS) deposited CdTe grains (which have a much higher substrate temperature) are quite small and activation treatment is needed also for increasing the grain size [3].

It is known that for a good cell performance an activation treatment is necessary. Generally to enhance the grain size and passivate the grain boundaries in the CdTe polycrystalline

structure a layer of CdCl₂ is deposited on top of the CdTe and then annealed in air.

The CdCl₂ treatment is, in our case, applied by preparing a saturated solution of CdCl₂ in methanol.

Few drops of solution are deposited on the CdTe layer and the stacks are annealed in air at a temperature ranging from 390 °C up to 430 °C for 30 min. Optimization of the device has brought to an optimum temperature of 410 °C. The number of drops of saturated solution is also an important factor in order to define the optimized quantity of CdCl₂ to have the right compromise between CdTe activation and excess in CdS/CdTe intermixing.

The Freon[®] treatment is a different method: an as-deposited cell is treated in a vacuum chamber at high temperature in a controlled mixture of chlorine containing gases (difluorochloromethane, HCFCl₂, Freon[®] R-22) and argon (with pressures from 10 mbar up to 60 mbar for Freon[®] and of 500 mbar for argon) for a time between 5 min and 25 min and at temperatures between 400 °C and 450 °C [3]. At around 400 °C Freon[®] dissociates, freeing chlorine, which is reacting with CdTe forming CdCl₂ which re-crystallizes the layer and passivates the grain boundaries [4].

2.4. Back contact

Back contact is made by vacuum evaporation of Cu/Au stacks, contacts are dots of 0.13 cm². Subsequently an air annealing of the back contact is applied at 200 °C in air for 20 min in order to diffuse Cu in CdTe and make an ohmic contact [5].

In the case of CdCl₂ treatment, a bromine–methanol etching is applied in order to remove the CdCl₂ layer and to prepare the surface for the Cu/Au deposition, however the removal of the CdCl₂ in the case of wet treatment is quite difficult [6]. In case of Freon[®] treatment, the treated CdTe is not etched since the surface is free from CdCl₂ (re-evaporated at high temperature in vacuum) and a tellurium rich layer is made during the activation process [4,6].

Deposition of copper results to be very sensitive, a higher amount of copper improves the back contact also doping the bulk CdTe but reduces the shunt resistance (R_{sh}) resulting in a lower fill factor. The amount of copper has been tuned for the differently treated CdTe layers, a more conductive absorber would need less copper to improve the performance.

3. Results and discussion

The grain growth, re-crystallization dynamics and the performance of the cells have been studied accordingly to the different parameters of the re-crystallization treatment as for example the ratio between Freon[®] and argon in the mixture or the treatment temperature and compared with the standard CdCl₂ process.

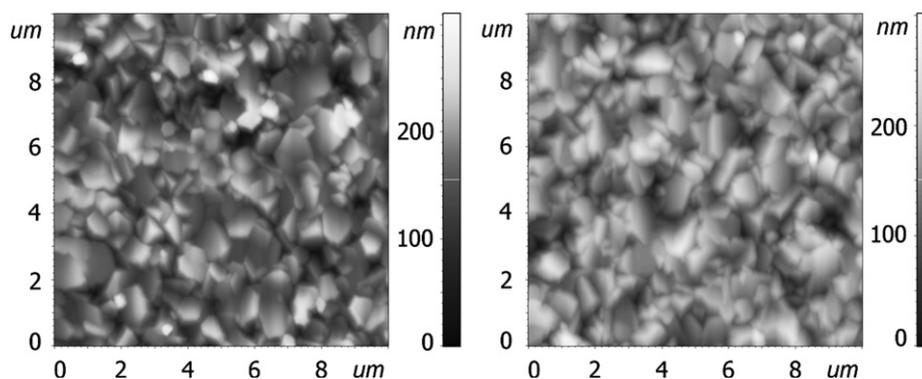


Fig. 1. AFM pictures of as-deposited CdTe on Cds/ZnO/ITO (left) and on Cds/ITO (right).

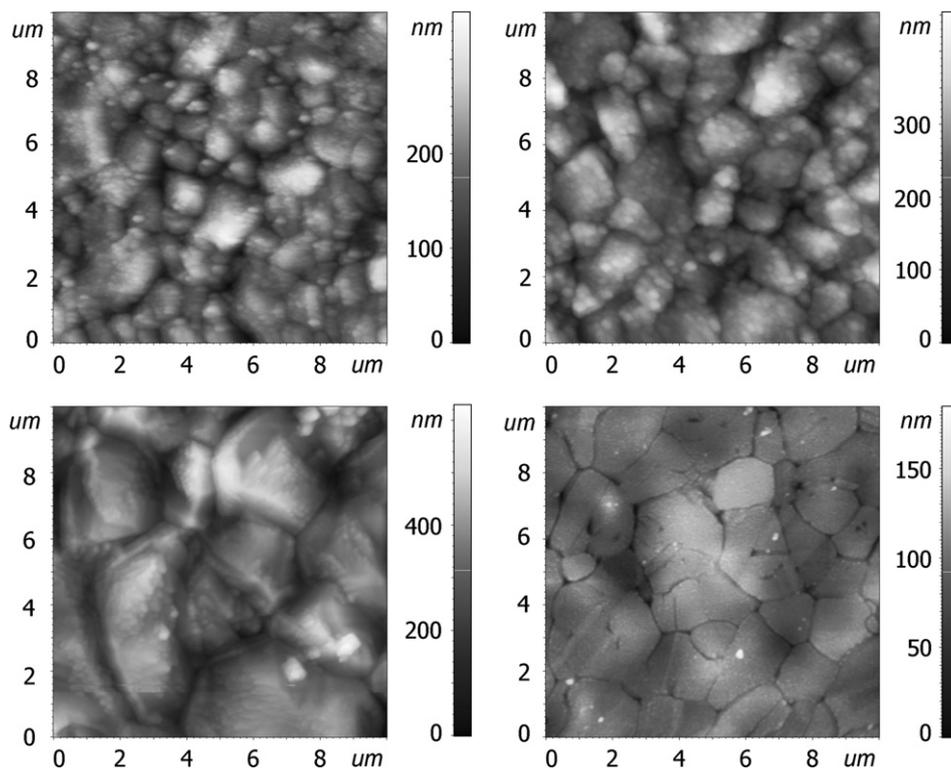


Fig. 2. AFM pictures of CdTe treated with Freon[®] and argon at 400 °C (left, top), 420 °C (right, top), 440 °C (left, bottom) and with CdCl₂ at 410 °C (right, bottom), in the last case the grains have been etched to remove CdCl₂ residues.

3.1. AFM analysis

After deposition at 300–340 °C, CdTe is treated in Freon[®] and argon atmosphere. Different partial pressures for Freon[®] and different treatment temperatures have been applied, and the recrystallized CdTe grains have been observed with a NT-MDT Solver-Pro Atomic Force Microscope with SMENA-A head in semi-contact mode.

In Fig. 2 AFM pictures of CdTe treated at temperatures from 400 °C to 440 °C are presented. The grain size is directly dependent on the annealing temperature: most of the grains are around 1 μm wide for 400 °C, 2 μm for 420 °C and up to 7 μm for 440 °C. Higher temperatures have also been applied but no significant increase of the grain size has been registered, so a saturation of the recrystallization process was registered.

Freon[®] treatment assures good re-crystallization of the grains but CdCl₂ treatment generates a more compact morphology, moreover similar grain sizes in the case of CdCl₂ treated samples are obtained for lower annealing temperatures (compare CdTe treated with CdCl₂ at 410 °C and CdTe treated with Freon[®] and argon at 420 °C Fig. 2).

Higher annealing temperatures are then needed in case of Freon[®] treatment for obtaining similar crystallization of the CdCl₂ treated layers.

3.2. XRD analysis

XRD measurements have been made in order to study the crystallization and re-crystallization process in the differently treated CdTe/CdS/TCO stacks.

X-ray-diffraction (XRD) data were taken with a Thermo ARL XTRA powder diffractometer, operating in Bragg–Brentano geometry equipped with a Cu-anode X-ray source (K_{α} , $\lambda=1.5418 \text{ \AA}$) and using a Peltier Si(Li) cooled solid state detector.

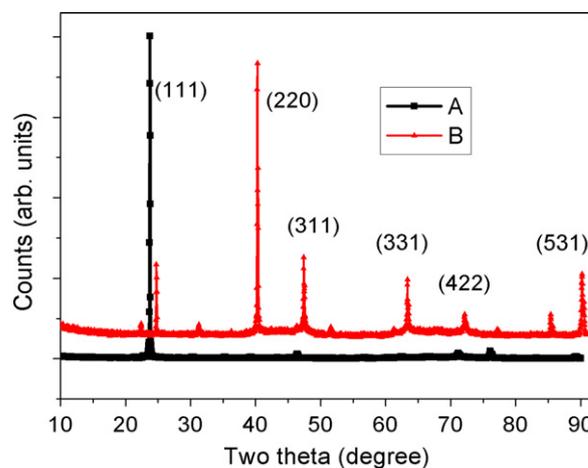


Fig. 3. XRD spectra of as-deposited CdTe on CdS/ZnO/ITO (top) and on CdS/commercial ITO (bottom).

The spectra address a dependence of the CdTe layer re-crystallization not only on the treatment temperature but also on the different TCO substrate, as already observed with AFM technique (shown in Fig. 1).

In Fig. 3, XRD spectra of as-deposited CdTe layer deposited on a stack of CdS/TCO are shown. CdTe crystals are strongly oriented as evidenced by the diffraction intensity of the (1 1 1) peak in comparison with the intensity of the other reflections. This preferential orientation is typical for polycrystalline as-deposited CdTe [5], in our case it is observed only for CdTe deposited on the CdS/commercial ITO substrate, while on the CdS/ZnO/ITO CdTe grows with a lower degree of orientation and with a different preferential direction.

As shown in Fig. 4, during activation treatment a re-crystallization process of CdTe on commercial ITO takes place with different relative

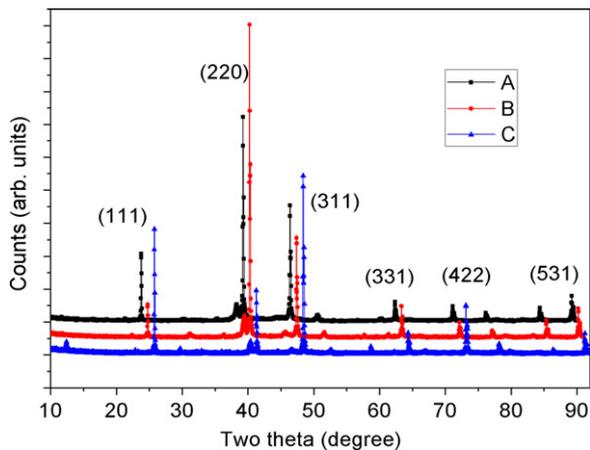


Fig. 4. XRD spectra of treated CdTe in argon+Freon[®] atmosphere at 420 °C (A), with CdCl₂ at 410 °C (B) and at 430 °C (C) on CdS/ZnO/ITO.

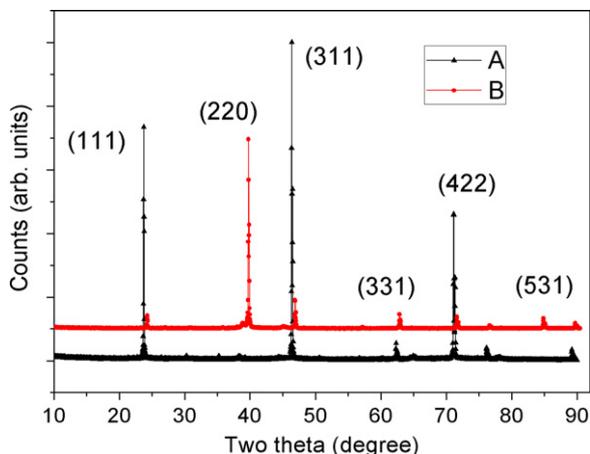


Fig. 5. XRD spectra of re-crystallized CdTe with Freon[®] treatment in only Freon[®] at (B) and argon+Freon[®] atmosphere (A) on CdS/commercial ITO.

growth rate of crystallite faces depending on the concentration of Freon[®] in the gaseous atmosphere. In fact, as a consequence of the treatment the as-deposited CdTe crystallites change their orientation as a function of the chlorine concentration. When CdTe on CdS/commercial ITO is annealed by a mixture of argon+Freon[®] the orientations: (2 2 0), (1 1 1) and (4 2 2) become the main diffraction peaks so that a much more randomized structure is generated.

For these samples we also have applied a treatment with low gas pressure (only 50 mbar argon instead of the standard 500 mbar argon plus 10 mbar Freon[®]) with pure Freon[®] not diluted in argon. This activation treatment shows a lower re-orientation of the grains with a non-randomized structure (see Fig. 5), it is worth mentioning that the orientation is exactly the one of the as deposited CdTe/CdS but on the ITO/ZnO stacks. This is evidence that CdTe deposited with this particular ITO/ZnO stack has a higher crystallization quality than the CdTe/CdS deposited on our commercial ITO.

When CdTe is deposited on CdS/ZnO/ITO, the orientations of the polycrystals are substantially different, even before the activation treatment, as observed above. As a matter of fact the main reflection is the (2 2 0) line and no substantial changes are detected for both CdCl₂ and Freon[®] treated layers. Only in the case of CdCl₂ treated samples at high temperature the crystals appear differently oriented (see increase of (3 1 1) reflection in Fig. 6(bottom)).

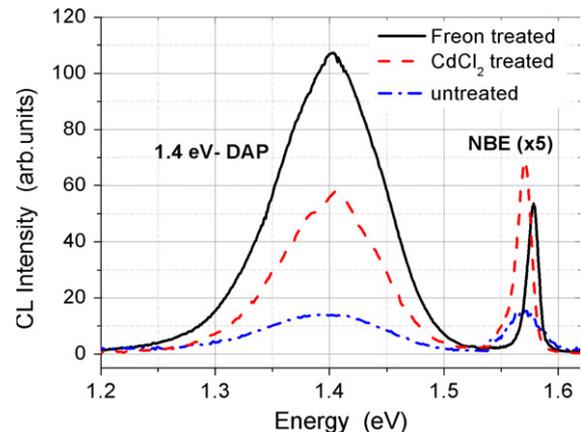


Fig. 6. Comparison among 77 K CL spectra of untreated, HCF₂Cl annealed at 420 °C and CdCl₂ based annealed CdTe, near band edge peaks have been magnified for clearness.

From this data, we observe that the nature and quality of the TCO substrate is not only essential in order to ensure a good efficiency of the devices but strongly affect the growth of the CdTe crystallites.

3.3. CL analysis

The effect of activation methods (Freon[®] or CdCl₂ process) and Freon[®] treatment parameters (temperature and time) on the CdTe radiative recombination properties were also studied by acquiring the cathode-luminescence spectra at 77 °K and electron beam energy (E_b) of 30 keV. The selected E_b guarantees a primary electrons maximum penetration depth of 2.8 μ m, as calculated by Monte Carlo simulations [7]. With these experimental conditions it is possible to collect information from the bulk CdTe, well below the sample surface.

The spectra in Fig. 6 show the typical CdTe spectroscopic features: two main CL bands are visible: the near band edge (NBE) emission, centred at about 1.58 eV, due to the excitonic recombinations and a broad band centred at about 1.4 eV, generally attributed to a donor-acceptor pair (DAP) which involves a Cl based complex (A-centre) as acceptor level in the transition [8].

The untreated CdTe presents a lower NBE intensity compared with samples deposited by CSS. This, together with a lower average grain size, is explainable by considering a lower crystalline quality and higher crystalline defects concentration, due to the lower substrate temperature.

The dramatic increase of the luminescence efficiency as shown in Fig. 6 is a clear evidence of the influence of the post-deposition treatments on CdTe. The NBE bands are plotted with high spectral resolution and their relative intensity normalized to the respective 1.4 eV band. The intensity of both the CL bands increases after any activation treatment (CdCl₂ or Freon[®]). As a matter of fact recrystallization enhances the crystalline quality of the material and consequently the radiative recombination efficiency. Cl doping from the HCF₂Cl [8], together with Cd vacancies, are considered the origin of A-centre. From this point of view the recrystallization effects are confirmed also for Freon[®] treatment; however, CdCl₂ treated CdTe shows the highest NBE intensity, corresponding to a better crystalline quality material.

Moreover a shift of the NBE peak is also observed, as reported by Halliday et al. [9] this can be attributed to a change from a shallow-donor bound to an acceptor bound exciton making the material p-type and increasing the carriers concentration.

3.4. *I–V measurements*

Several photovoltaic devices have been made with different parameters of both CdCl₂ and Freon[®] treatment for CdTe deposited on the different stacks described before.

The highest performance was given by CdCl₂ treated cells and with stronger CdS/TCO stacks, this means that the most performing TCO was the one made with high temperature deposited ZnO/ITO with enhanced ability and prevention of sodium and indium diffusion. Moreover only 2 nm of copper with 50 nm of gold are necessary for a good contact. With this configuration efficiencies exceeding 10% are routinely obtained.

If Freon[®] treatment is applied, much lower efficiencies are measured: highest efficiencies are obtained with 8 nm of copper; however, a much lower shunt resistance (R_{sh}) gives lower fill factors and lower open circuit voltages.

If a 2 nm copper contact is applied on these Freon[®] treated cells a very low efficiency is performed (see Fig. 7). Anyway with more aggressive Freon[®] treatment (by higher Freon[®] partial pressures or higher temperature) bigger grain size is obtained but not higher efficiencies, excess of Freon[®] pressure have resulted in shunted device. So the required copper amount is also depending on the different CdTe treated layer, we have registered that in case of Freon[®] treated CdTe devices four times the amount of copper is needed for a reasonable efficiency compared to the CdCl₂ treated cells. Moreover a very strong roll-over is registered in case of Freon[®] treated cells, we believe this is not connected to the back contact design, since the same back contact does not provide such a high roll-over on CdCl₂ treated cells and since also different additional bromine–methanol etchings have been applied without any change.

The reason for this roll-over has to be most probably attributed to the electrical properties of the absorber that would increase the energy barrier of the back contact.

This is consistent with the fact that activation by Freon[®] is much weaker than the one made with CdCl₂ as reported above. On the other hand using a lower amount of copper allows to have a better working cell and this results in a higher efficiency, as shown in the next section.

Cells made with CdCl₂ treatment exhibit efficiencies from 10% to 11%, with current in the range of 22 mA/cm² to 25 mA/cm², V_{oc} exceeding 750 mV and FF from 60% to 70%. The relatively low V_{oc} and FF are connected with relatively low R_{sh} . This can be explained by an excessive consumption of CdS into the CdTe layer. The best results were obtained with thicker CdS (more than 500 nm) annealed in vacuum at 450 °C (see curve number 4 in Fig. 7).

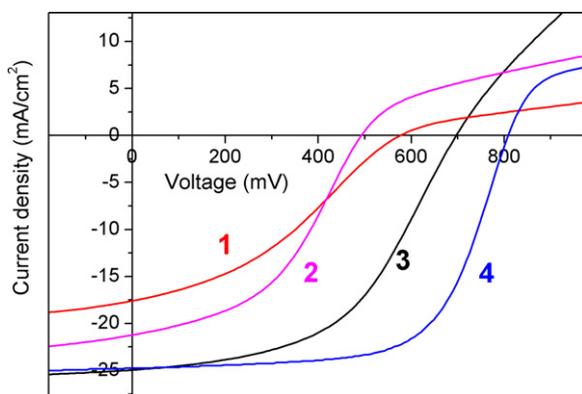


Fig. 7. *I–V* measurement of solar cells with different treatments and back contacts (see also Table 1) (1) only Freon[®] treated CdTe (8 nm copper); (2) Freon[®] + Ar treated CdTe (2 nm copper); (3) Freon[®] + Ar treated CdTe (8 nm copper); (4) CdCl₂ treated CdTe (2 nm copper).

Table 1
Best cells performance.

N	Treatment type	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	η (%)	Cu (nm)
1	Freon [®]	578	17.6	35.3	3.6	8
2	Ar + Freon [®]	493	21.2	44.8	4.7	2
3	Ar + Freon [®]	697	24.9	50.2	8.7	8
4	CdCl ₂	790	22.4	64	11.3	2

Freon[®]-treated cells show lower efficiencies than CdCl₂ treated ones. The highest achieved efficiency for this treatment is 8.7% (see curve 3 in Fig. 7). Although the Freon[®] treated cells would not need a post deposition etching [2], a good ohmic back contact was not easily reproducible. Many of our Freon[®]-treated cells have shown a kink on the positive part of the curve (Fig. 7 cell1, 2). Parameters of shown curves are presented in Table 1.

3.5. *Transport properties.*

For device characterization two different type of cells made with vacuum evaporation were taken into consideration: one activated by Freon[®] and one activated by CdCl₂. In order to avoid a poor back contact that would not allow a reasonable electrical characterization, back contacts for Freon cells were prepared with 8 nm of copper while for CdCl₂ cells with 2 nm of copper. Gold was 50 nm for both kinds of samples. However *C–V* measurements are usually taken avoiding high forward bias in order not to be influenced by the back contact capacitance.

Moreover cells made by close space sublimation at the university of Parma, which were successfully activated by HCF₂Cl gas, with efficiencies exceeding 10% were taken as a reference with the low temperature deposited cells.

Dark current–voltage with relation to temperature (*I–V–T*) characteristics for all cells were measured in the range 300–360 K and the sample was either placed in a liquid nitrogen-cryostat or on a Peltier-controlled substrate holder. Where possible, the saturation current I_0 and the diode ideality factor A were extracted by fitting the single diode equation with series (R_s) and shunting (R_{sh}) resistances:

$$I(V) = I_0(\exp(q(V - IR_s)/kT) - 1) + (V - IR_s)/r_{sh} \text{ where}$$

$$I_0 = I_{00} \exp(-\Phi_b/kT)$$

where Φ_b stands for a diode barrier height, I_{00} is a weak temperature dependent pre-exponential factor, k —the Boltzmann constant and T —the measurement temperature. The meaning of parameters I_0 , Φ_b and A depends on the transport mechanism [10], [11]. It was found that for all three samples the ideality factors do not depend on the temperature and exhibit the values between 1.5 and 1.6. Low dependency of A on the temperature indicates a dominant Shockley–Read–Hall recombination process in the bulk region [10, 12] and allowed us to construct the modified Arrhenius plots (not shown here), in both vacuum evaporated cells the barrier height was nearly the same, $\Phi_b \sim 1.35$ eV (± 0.1 eV systematic error).

3.6. *Space charge profiles.*

A standard technique which is very often applied for determination of the doping level in semiconductor junctions is capacitance–voltage (*C/V*) profiling. However, in the presence of deep levels free carrier concentrations determined by *C/V* profiles can be subjected to large errors [13]. This can be overcome by drive level capacitance profiling (DLCP), as DLCP is a fully dynamical measurement giving undistorted doping distributions. For junctions without deep traps adjusting their charge state to

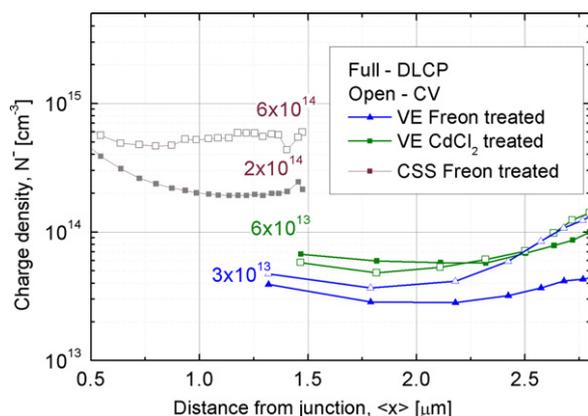


Fig. 8. C/V (open) and DLCP (full) space charge profiles (scale is reduced for clearness). The estimation of free hole concentrations is indicated in the figure.

the DC bias, DLCP and C/V profiles coincide, so the difference between the C/V and DLCP profile gives a lower bound for deep defect concentration active in a given measurement conditions (i.e., temperature and frequency) [14].

The capacitance measurements were performed with an Agilent E4980A LCR meter controlled by LabView via computer. Space charge distributions measured by C/V (open symbols) and DLCP (full symbols) at room temperature (RT) and 10 kHz are shown in Fig. 8. Doping concentrations in the space charge region (SCR) of CSS-Freon[®], VE-CdCl₂ and VE-Freon[®] samples were estimated to be $2 \times 10^{14} \text{ cm}^{-3}$, $6 \times 10^{13} \text{ cm}^{-3}$, $3 \times 10^{13} \text{ cm}^{-3}$, respectively, as indicated in the figure by the lowest values of the DLCP curves. Deep defects contributing to capacitance–voltage profiles were also detected. The difference between the C/V and DLCP profile, indicating the lower bound for the concentration of deep defects following the DC bias sweep, is also the highest for the CSS-Freon[®] sample (circles) and amounts $4 \times 10^{14} \text{ cm}^{-3}$. For the VE-Freon[®] device (triangles) the defect concentration varies from $1 \times 10^{13} \text{ cm}^{-3}$ at $2 \mu\text{m}$ up to $2.3 \times 10^{14} \text{ cm}^{-3}$ at distances larger than $2.5 \mu\text{m}$. In the VE-CdCl₂ sample (squares) we detected no large differences between the C/V and DLCP profiles around RT.

4. Conclusions

Two different activation treatments were applied in order to understand their effect on the thin film solar cells deposited with low substrate temperature deposition process. More compact CdTe was obtained on ITO+ZnO stacks. The XRD measurements reveal that the pure Freon[®] (without argon) activation treatment of the CdTe on CdS/commercial ITO gives rise to a crystallized layer very similar to that one present in the as deposited CdTe on CdS/ZnO/ITO.

This shows that crystallization for CdTe deposited on CdS/ZnO/ITO is similar to the one weakly treated CdTe on CdS/commercial ITO, showing that we start from a better crystallization rate if the ZnO/ITO layers deposited at high temperature are used and also shows that with low pressure in the Freon[®] treatment the effect is smaller than the case when Freon[®] is mixed with argon at higher pressure rates.

CdTe deposited on CdS/commercial ITO stacks lose preferred orientation during both CdCl₂ and Freon[®] treatments. CdTe deposited on CdS/ZnO/ITO stacks keeps the (2 2 0) preferential orientation for both CdCl₂ and Freon[®] treated layers and only in the case of high temperature CdCl₂ treatment the crystals are more randomly oriented. This can be explained by higher stability and better crystalline quality of CdTe films deposited on ITO+ZnO stacks.

In case of Freon[®] treated CdTe, four times more amount of copper is needed for good efficiencies compared to the CdCl₂ treated cells. This can be explained by lower capacity of Freon[®] treatment to activate the absorber layer and so an additional doping of CdTe with copper is necessary, confirmed by capacitance–voltage analysis which shows a reduced carrier concentration for these devices. Moreover cathodoluminescence measurements on the CdTe show a very strong difference in luminescence efficiency, meaning an enhancement of the $V_{\text{Cd-Cl}}$ complex (A-centre) concentration for CdCl₂ treated samples.

Difluorochloromethane treatment for CdTe deposited by low substrate temperature processes shows to be less effective in improving the electrical parameters of the absorber, since a strong difference between the change of the structural properties (similar to the CdCl₂ treated cells) and the enhancement of the electrical properties (very much different from the CdCl₂ treated cells) is observed. This shows that there is an evidence of disconnection in the electrical and morphological properties: enhancement of the grain size and reduction of grain boundaries does not allow itself automatically to increase carrier concentration and improve the junction properties.

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