

# A study of the CdTe treatment with a Freon gas such as $\text{CHF}_2\text{Cl}$

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## Abstract

In order to obtain high efficiency CdS/CdTe solar cells, a CdTe heat treatment in a  $\text{Cl}_2$  containing atmosphere is necessary. Normally, this treatment is done by depositing a  $\text{CdCl}_2$  thin film on top of CdTe and by heating the system in air at a fixed temperature. This step is disadvantageous in a large scale fabrication process because it involves the use of  $\text{CdCl}_2$  that it is difficult to be handled. We replaced this treatment by using a gas ( $\text{HCF}_2\text{Cl}$ ) that is stable, inert and not toxic at room temperature and eliminates the step of  $\text{CdCl}_2$  evaporation and subsequent chemical etching.

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## 1. Introduction

Recently, we obtained CdTe solar cells with efficiencies close to 16% by using a simplified growth process suitable to be scaled-up for an industrial production [1]. A crucial step to get high efficiency CdTe solar cells is the thermal treatment carried out in presence of Chlorine. Usually, this treatment is made by depositing on top of the CdTe surface a  $\text{CdCl}_2$  thin film by vacuum evaporation or by dipping CdTe films in a methanol solution containing  $\text{CdCl}_2$  and by heating the system in Ar or air atmosphere at a temperature of about 400 °C for 8–20 min; after that, an etching is usually made to remove some  $\text{CdCl}_2$  residuals and oxides and to leave a Te-rich CdTe surface. This etching is usually carried out with a Br-methanol solution or by using a mixture of  $\text{HNO}_3$  and  $\text{HPO}_3$ . In view of an industrial production, the use of  $\text{CdCl}_2$  has some drawbacks. Firstly, since  $\text{CdCl}_2$  has a quite low evaporation temperature (about 500 °C in air), it cannot be stored in large quantity since it can be dangerous in case of fire because of Cd release in the environment. Secondly,  $\text{CdCl}_2$  is soluble in water and, as a consequence, severe measures must be taken to preserve environmental pollution and health damage. Finally, the use

of chemical etchings, such as  $\text{HNO}_3$  and  $\text{HPO}_3$  or Br-Methanol solution, implies two problems: the first one is related with the workers safety in the factory and the second one concerns their disposal after use. In order to avoid some of the drawbacks described above, we have substituted  $\text{CdCl}_2$  with a gas belonging to the Freon family and containing Chlorine, such as difluorochloromethane ( $\text{HCF}_2\text{Cl}$ ). This gas is stable and inert at room temperature and it has not any toxic action. Moreover, we eliminated any chemical etching by substituting it with a vacuum annealing. The only drawback in using a Freon gas could be that it is an ozone depleting agent, but, in an industrial production, it can be completely recovered and reused in a closed loop.

## 2. Experimental details

A CdS/CdTe based solar cell is composed by four parts, as shown in Fig. 1. The front contact, namely the Transparent Conducting Oxide (TCO), is made by two layers: 400 nm thick ITO and 300 nm thick ZnO films. The first one has a sheet resistance of about 5  $\Omega/\text{Sq}$ , while the second one has a resistivity on the order of  $10^3 \Omega\text{cm}$ . The role of ZnO layer is both to hinder the In diffusion from ITO and to separate CdS from ITO in order to limit the effect of eventual pinholes that could be present in CdS [2]. The window layer, that is Cadmium Sulphide (CdS), has a

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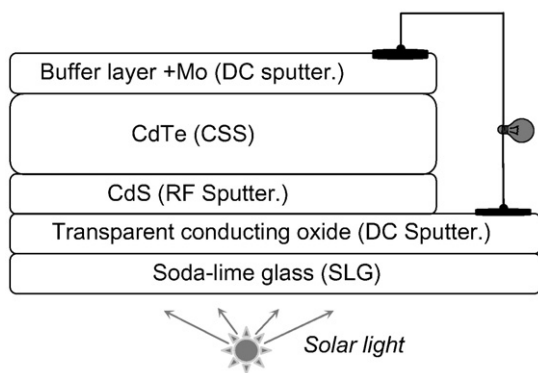


Fig. 1. Scheme of the structure of the CdTe/CdS thin film solar cell.

80 nm nominal thickness and it is deposited by RF-Sputtering in Ar+CHF<sub>3</sub> atmosphere. The CdTe absorber layer is deposited by Close-Spaced Sublimation (CSS) at a substrate temperature of 500 °C in Ar atmosphere (1–10 mbar). The deposition rate is about 2 µm/min. The thickness of CdTe films is normally in the range of 6–8 µm. The back contact is composed by two layers: a buffer layer and a Mo film. Both of them are deposited by Magnetron DC-Sputtering in Ar atmosphere. The buffer layer is important to guarantee the ohmic behaviour of the back contact and makes solar cells more stable without affecting efficiency.

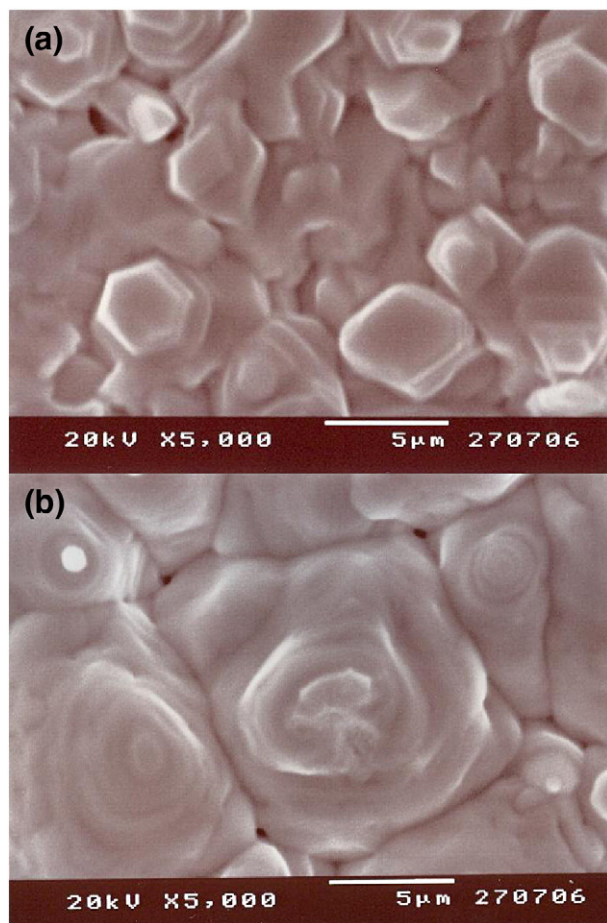


Fig. 2. CSS-CdTe film SEM plan view. (a) Untreated CdTe and (b) treated CdTe in Ar+HCF<sub>2</sub>Cl atmosphere at 400 °C for 5 min.

The TCO/CdS/CdTe system prepared as described above is placed in an evacuable quartz ampoule. Before each run, the ampoule is evacuated with a turbo-molecular pump up to 10<sup>−6</sup> mbar. As a source of Cl<sub>2</sub>, a mixture of Ar+CHF<sub>2</sub>Cl is used. The pressure range varies between 30 and 50 mbar for CHF<sub>2</sub>Cl and 400 mbar for the Ar+CHF<sub>2</sub>Cl total pressure. These pressures are independently measured by two different capacitance vacuum gauges and monitored by a Varian MultiGauge. The quartz tube is put into an oven where a thermocouple is installed in order to control the furnace temperature, which is in the range of 380–420 °C. The annealing time is 10 min for all samples studied in this work. After the treatment, a vacuum for about 10 min, keeping the temperature at 400 °C, is done in order to allow the CdCl<sub>2</sub>, formed on the CdTe surface, to re-evaporate and to obtain a clean CdTe surface ready for the back contact. The images of the surface morphology are realized by a Cambridge

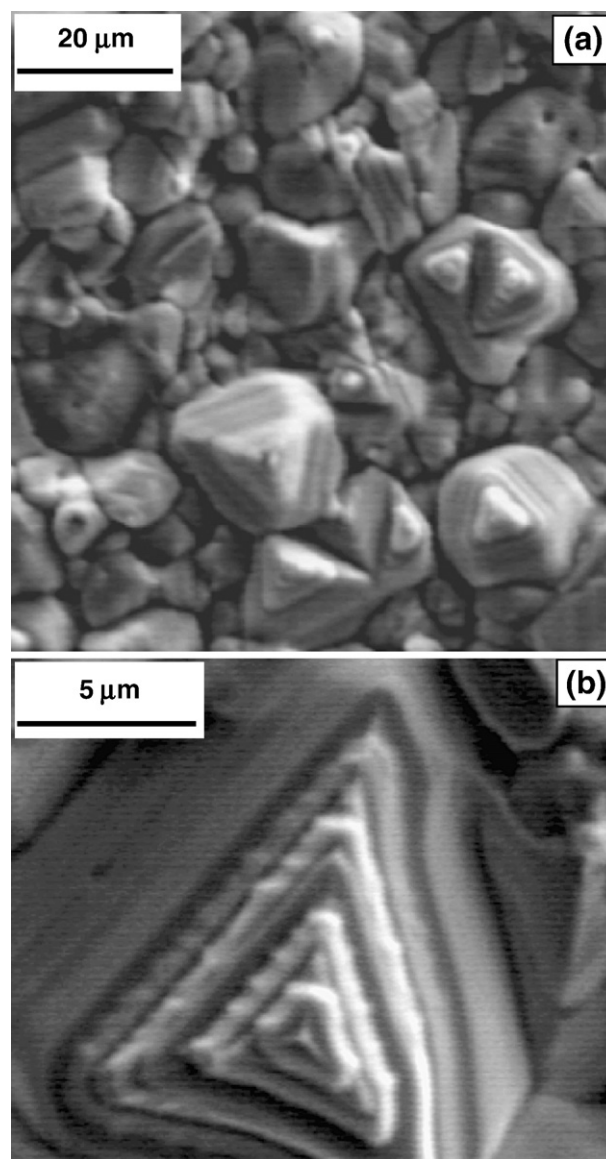


Fig. 3. (a) CdTe SEM plan view for a treated CdTe in 400 mbar Ar+HCF<sub>2</sub>Cl total pressure and 40 mbar HCF<sub>2</sub>Cl partial pressure at 400 °C for 10 min, (b) enlargement of the previous image in which is clearly visible how the Freon treatment acts as a chemical etching as well.

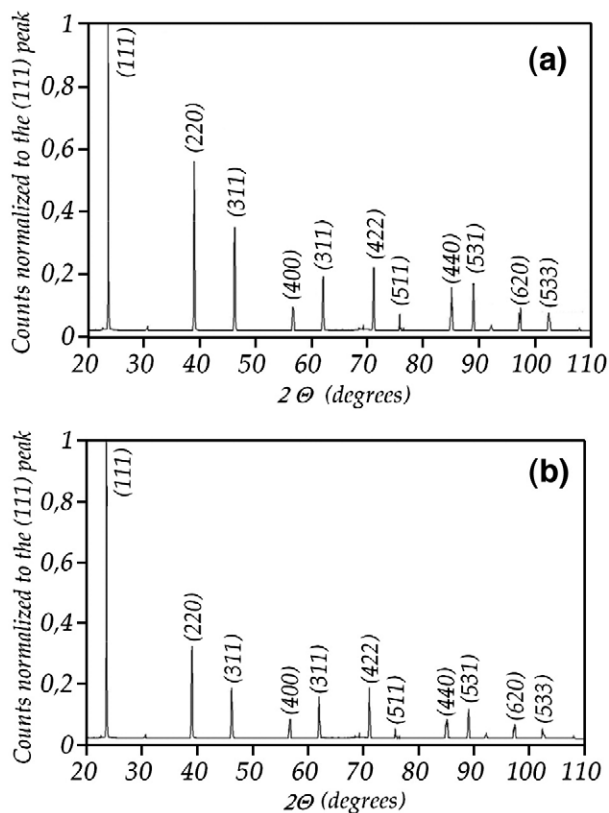


Fig. 4. XRD of CSS-CdTe film (a) before and (b) after treatment.

S-360 scanning electron microscope (SEM). The luminescence analyses are performed by a Gatan MonoCL system mounted on the SEM. The CL spectra as well as the monochromatic CL images are acquired using a dispersion system equipped with two diffraction gratings and a system of a multi-alkali (Hamamatsu) photomultiplier and an Edinburgh liquid nitrogen cooled Ge detector. The dark conductivity and the activation energy as a function of temperature (84–300 K) were performed by using a Keithley 236 source measure unit. The temperature was set by a system DL 4600 Bio-Rad microscience division. Samples, to perform this measurement,

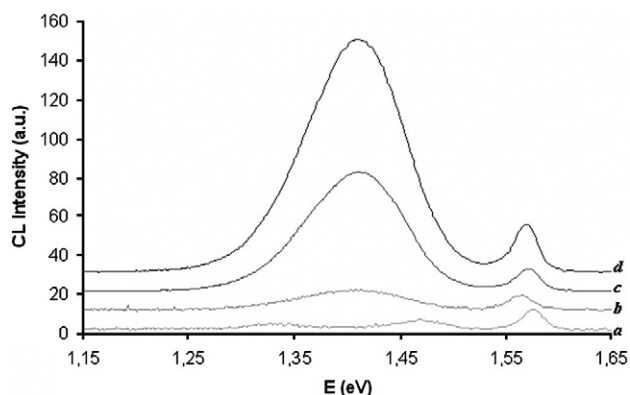
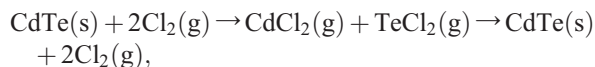


Fig. 5. Comparison of the CL spectra acquired from (a) not treated CSS-CdTe and treated CSS-CdTe in 400 mbar Ar+CHF<sub>2</sub>Cl atmosphere for 10 min using (b) 0 mbar, (c) 40 mbar and (d) 50 mbar HCF<sub>2</sub>Cl partial pressure.

were composed by ZnO (300 nm), CdTe (~7 μm) and the back contact.

### 3. Results and discussion

During the heat treatment at about 400 °C, CHF<sub>2</sub>Cl decomposes and CdTe starts to evaporate, then a reaction involving chlorine in gaseous phase takes place [1]:



This reaction favours CdTe film re-crystallization and enhances its crystalline quality. During the above reaction, a

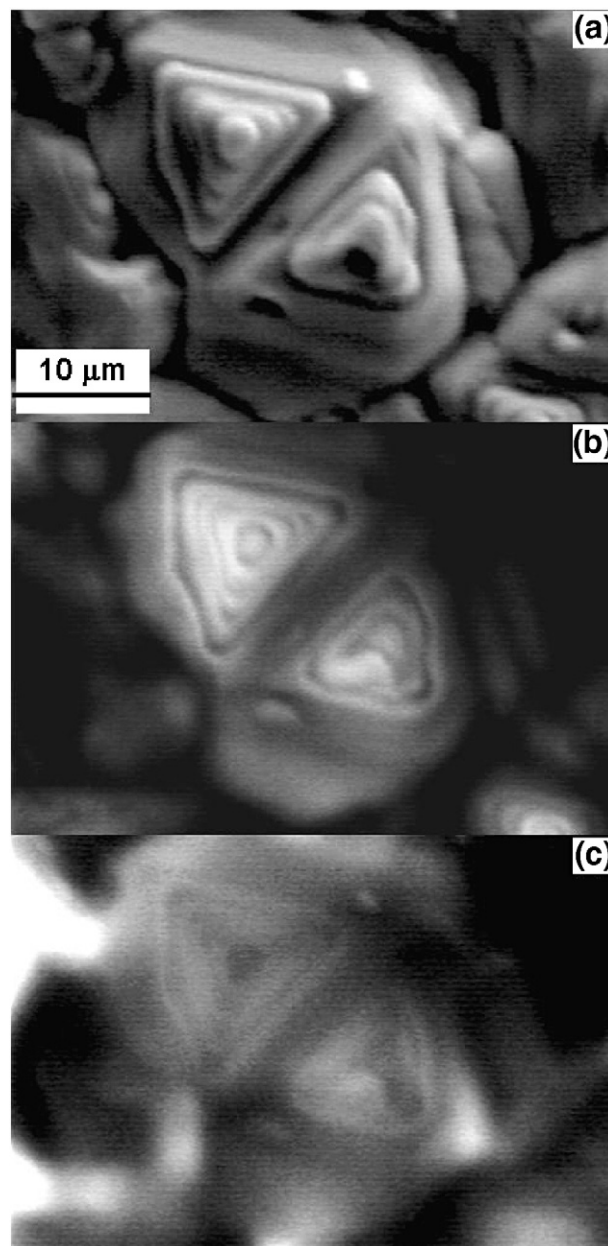


Fig. 6. Comparison between (a) SEM image, (b) monoCL taken at 1.57 eV and (c) monoCL taken at 1.4 eV for a treated CdTe with 40 mbar partial pressure of CHF<sub>2</sub>Cl.



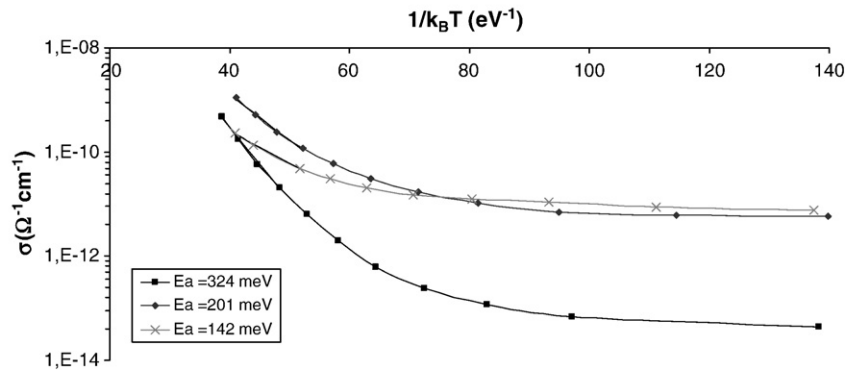


Fig. 7. Arrhenius plot of  $\sigma$  (Ω<sup>-1</sup> cm<sup>-1</sup>) versus  $1/k_B T$  (eV<sup>-1</sup>). (■) not treated CdTe, and treated CdTe with respectively (◆) 30 mbar and (×) 40 mbar HCF<sub>2</sub>Cl partial pressure. Energies activation ( $E_a$ ) are also shown.

small amount of solid CdCl<sub>2</sub> could also be formed on the CdTe surface. The small grains, which are the more instable, are the first one to go in vapour phase. In this condition, transport phenomena happen and CdTe re-grows because it re-deposits when it is very close to a surface of a stable grain. This treatment is able to increase grain size and to eliminate small grains. CdTe re-crystallization after the treatment is shown in Figs. 2 and 3. Fig. 2 shows CdTe morphology before (Fig. 2-a) and after (Fig. 2-b) the Chlorine treatment. Before treatment, grains exhibit a hexagonal structure and an unhomogeneous distribution of their dimensions. After treatment, Fig. 2-b, it is clearly visible that grains are bigger than before and they show a pyramid-like structure with a hexagonal base. The other aspect is that small grains disappear. From Fig. 3-a and b, it can be seen how, after the annealing, grains appear pyramid-like and that some erosions are present. The good re-crystallization of the film is also visible by XRD measurements. CdTe grains exhibit a zincblende structure, but after the annealing in Freon atmosphere, the system tends to have a more preferential orientation along the (111) direction since the other peak intensities tend to decrease. This is shown in Fig. 4. In addition to the grain enlargement and the better crystallization of CdTe films, the Freon treatment influences the cathode-luminescence (CL) emissions. In Fig. 5, the comparison among CL spectra, performed at the liquid nitrogen temperature, of four different films, treated with different Freon partial pressures are shown. It can be observed that the total luminescence efficiency increases as a function of the Freon partial pressure. In addition, besides the band edge emission at about 1.57 eV, a broad CL peak at 1.4 eV, not present in the untreated sample, appears with an intensity that increases by increasing the Freon partial pressure during the CdTe treatment. The peak at 1.4 eV could be attributed to the A-centre due to a complex formed by a Cd vacancy ( $V_{Cd}$ ), that, as it is known, is a CdTe films native defect, and a Cl or F impurity which can diffuse into CdTe during the treatment [3,4]. The lateral distribution of the different CL emissions is investigated by acquiring monochromatic CL images at 1.4 eV and 1.57 eV, as shown in Fig. 6. For comparison a SEM image of a CdTe grain is shown in Fig. 6-a. Fig. 6-b is the 1.57 eV monoCL image of a treated CdTe grain. As it can be seen, a large part of the image is bright, which is a

proof of a good crystalline quality. In Fig. 6-c a monoCL image at 1.4 eV is shown. Also in this case, a good luminescence response can be seen. This suggests that some Cl (or F) impurities are incorporated also inside the CdTe grains, where the high  $V_{Cd}$  concentration could favour the formation of the A-centre. A level that could be attributed to the  $[V_{Cd}-Cl]$  complex is also seen by the Arrhenius plot of the CdTe dark conductivity as a function of the inverse of the temperature (Fig. 7). From this plot it can be seen that, in the case of not treated CdTe, the activation energy ( $E_a$ ) is proper of a level due to the presence of occasional impurities like Cu, Ag, and Au; in case of the treated CdTe, it can be seen that the  $E_a$  decreases by increasing the Freon partial pressure. The  $E_a$ 's relative to treated CdTe are lower than in the previous case and could be attributed to  $[V_{Cd}-Cl]$  complex [5]. The  $E_a$  decreasing by increasing the Freon partial pressure could be due to the enlargement of a band formed by the above complex.

#### 4. Conclusions

In this paper, we have studied a new CdTe treatment to get high efficiency CdTe/CdS solar cells. We do not use neither chemical etching nor CdCl<sub>2</sub>, but a chlorine containing gas such as CHF<sub>2</sub>Cl that it is not toxic and more suitable for a large scale production. In this work, it is demonstrated how this treatment acts as well as CdCl<sub>2</sub> treatment. It has been seen by SEM and XRD measurements how this treatment improves CdTe crystalline quality by enlarging grains and by the system tendency to get a better preferential orientation. It has also been seen the formation of a level by CL and conductivity measurements which could be attributed to a  $[V_{Cd}-Cl]$  complex. CdTe/CdS solar cells made by using CHF<sub>2</sub>Cl as a Chlorine source for CdTe treatment exhibit efficiencies close to 16% [1].

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