Study of MgCl$_2$ activation treatment on the defects of CdTe solar cells by capacitance-voltage, drive level capacitance profiling and admittance spectroscopy techniques

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ABSTRACT

CdTe solar cells have recently reached its highest conversion efficiencies, comparable to CuInGaSe$_2$ and Si devices. One of the key factors for the success of these devices is the so-called "activation" treatment, which typically consists in depositing a CdCl$_2$ film on the CdTe absorber layer and in a subsequent annealing in air or nitrogen atmosphere. Nevertheless CdCl$_2$ is a carcinogenic and water-soluble compound; for this reason recent studies have found MgCl$_2$ as a good alternative.

In this work we have studied devices (exceeding 14% efficiency) prepared by low-substrate temperature CdTe deposition and activated with MgCl$_2$ treatment (applied by wet deposition). The devices were characterized by means of current-voltage, capacitance-voltage, drive level capacitance profiling and admittance spectroscopy techniques. Carrier concentration and also concentration and distribution of shallow and deep defects are presented and compared with data obtained from analogous devices but activated with the standard CdCl$_2$. Despite CdTe layers treated with the two different processes exhibit similar structural properties, the distribution of deep and shallow defects results to be different and moreover admittance spectroscopy technique reveals the presence of different defects, at 344 and 358 meV, which are present only in MgCl$_2$ treatment case.

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1. Introduction

CdTe-based solar cell has demonstrated to be so far one of the best thin film photovoltaic technologies, reaching laboratory conversion efficiencies of more than 22% [1]. One of the most important step in the fabrication of high efficiency devices is the activation treatment of the CdS/CdTe junction: deposition of CdCl$_2$ followed by a high temperature annealing [2]. Nevertheless CdCl$_2$ is a highly toxic and carcinogenic chemical agent and for this reason its usage and disposal needs strong safety procedures. For this reason alternative activation treatments have been experimented and among them MgCl$_2$ treatment is one of the most successful option, reaching conversion efficiencies of about 15% [3]. MgCl$_2$ is a non-toxic chemical and its usage does not need special and strict restrictions. However so far at laboratory scale, solar cells treated with MgCl$_2$ have not reached the efficiencies of the world record CdCl$_2$-treated ones and for this reason CdCl$_2$ is still preferred. In order to better understand the MgCl$_2$ treatment mechanism and the reasons for its lower efficiency, two sets of CdTe-based solar cells have been fabricated

with our usual process [4]. One set has been activated with the standard CdCl$_2$ treatment, while the other one with MgCl$_2$ treatment. The solar cells have been electrically characterized by means of current-voltage (J-V), capacitance-voltage (C-V), drive level capacitance profiling (DLCP) and admittance spectroscopy (AS) techniques and the results for the two sets have been compared in order to address the differences in terms of electrical properties.

2. Experimental procedure

CdTe solar cells have been fabricated in superstrate configuration. The front contact is deposited on top of a 3 × 3 cm^2, 4 mm thick, soda-lime glass and it is produced as ITO/ZnO bi-layer stack. A 400 nm thick indium tin oxide (ITO) film is deposited by a customized RF reactive magnetron sputtering system, starting from a 90% In$_2$O$_3$:10% SnO$_2$ target. The film is deposited in a reactive atmosphere of Ar + 2–3% O$_2$ at a substrate temperature of 400 °C. The front contact is completed by covering the ITO layer with a 100 nm thick i-ZnO film, with the same sputtering machine, starting from a metallic Zn target, in a reactive atmosphere of Ar + 10–20% O$_2$ at a substrate temperature of 400 °C. The front contact is then covered with a CdS layer, which is deposited by high vacuum thermal evaporation. Also in this case the deposition system used is a customized one. Pieces of sintered CdS are put into a

tungsten crucible and heated up, in order to obtain a vapour flux corresponding to a deposition rate of about 1 nm per second. The CdS film is deposited at a substrate temperature of 100 °C, with a thickness of 200–300 nm. The p-n junction is completed depositing the CdTe film in the same deposition machine, again by vacuum evaporation. A graphite crucible is filled with CdTe crystals and heated up, obtaining a vapour flux rate of about 20 nm per second. In these conditions CdTe deposition takes place at a substrate temperature of 340 °C, until a film thickness of about 5–6 μm is reached. As already mentioned, two different activation treatments are applied after CdTe deposition and both consist in dissolving the activating agent ($CdCl_2$ or $MgCl_2$) in methanol, applying a specific amount of the resulting solution on the CdTe surface and annealing the stacks in air. The solutions have been prepared with different concentration levels and applied in form of drops, deposited onto the sample surface, in microliter volumes. The annealing in air of the sample is performed at temperatures ranging between 365 and 410 °C, for about 30 min. After the application of the activation treatment it is possible that some solution residuals remain on the CdTe surface, altering the electrical contact between the CdTe and the final back contact. In order to prevent this, an etching with Br-methanol solution is performed, which also promotes the formation of a p^+ Te rich layer on the CdTe surface. The back contact is produced by depositing a 2 nm thick Cu and a 50 nm thick Au films by vacuum evaporation at room temperature, using a customized high vacuum thermal evaporator starting from pure metallic shots. In order to allow Cu to better interact with the Te rich surface, the device is annealed in air at 190 °C for 20 min.

3. Results and discussion

3.1. J-V

To understand the effect of the $MgCl_2$ treatment with respect to the $CdCl_2$ one, we decided to compare cells made with the same process but with different activation conditions. In the case of $CdCl_2$, samples have been prepared using $CdCl_2$ solution of different concentrations, namely 20%, 30% and 50% of saturation and different volumes, from 60 to 300 μl. In Table 1 the main results obtained with this process are summarized. The J-V characterization has been performed using a self-modified solar simulator, equipped with a specific Osram Decostar 51 Eco Superstar (35 W, 550 lm) halogen lamp, calibrated with a Si solar cell. Samples have been measured under 100 mW/cm² irradiance, in 1.5 air mass (A.M.) and 25 °C conditions, by means of an A.M. 1.5 optical filter and a 25 °C thermalized metal plate. Data have been recorded by using a Keithley source meter 2420.

Best results have been found in using 150 μl of a 50% saturated $CdCl_2$ solution, which have been set as our reference values for the $CdCl_2$ sample. The reference sample exhibited an efficiency of 15,6% (Voc = 859 mV, Jsc = 25,6 mA/cm2, FF = 71%). A similar approach has been followed also in the case of $MgCl_2$ and the main results for this second process are shown in Table 2.

In this case, a champion cell with 14,3% efficiency (Voc = 852 mV, Jsc = 23,6 mA/cm2, FF = 71%) has been obtained by treating the sample with 140 μl of the 20% $MgCl_2$ saturated solution. Even if

Table 1
Photovoltaic parameters of solar cells treated with different $CdCl_2$ solutions.

$CdCl_2$-sample treatment	J_{SC} (mA)	V_{OC} (mV)	FF (%)	η (%)
20% $CdCl_2$ 150 μl, 410 °C	17,3	803	58,3	8,1
30% $CdCl_2$ 300 μl, 390 °C	23,7	831	66,1	13
50% $CdCl_2$ 150 μl, 380 °C	25,6	859,3	70,9	15,6

Table 2
Photovoltaic parameters of solar cells treated with different $MgCl_2$ solutions.

$MgCl_2$-sample treatment	J_{SC} (mA)	V_{OC} (mV)	FF (%)	η (%)
20% $MgCl_2$ 100 μl, 380 °C	23,7	788,9	66,1	12,4
20% $MgCl_2$ 200 μl, 380 °C	23,4	760,8	59,8	10,6
50% $MgCl_2$ 60 μl, 380 °C	23,7	838,2	65,5	13
50% $MgCl_2$ 200 μl, 395 °C	23,2	781,9	62,7	11,4
20% $MgCl_2$ 140 μl, 380 °C	23,6	852,3	71.1	14,3

solar cells fabricated with the two processes have similar conversion efficiencies, the ones treated with $CdCl_2$ have reached higher photovoltaic parameters.

3.2. C-V/DLCP

Samples have been characterized also by C-V and DLCP measurements, in order to obtain a correlation between the treatment parameters and their effect on the electrical properties of the devices. These measurements have been performed in a Janis cryostat with an HP 4284 A LCR meter, at a pressure of 10^{-4} Pa and with a Lakeshore 325 system temperature controller. Measurements have been done at temperatures ranging from 200 K to 300 K and at frequency values of 10 kHz, 100 kHz and 1 MHz for studying the defect response evolution.

In Fig. 1 a comparison of representative C-V/DLCP spectra are shown. Data were collected at a frequency of 10 kHz, with samples respectively treated with (A) 100 and (C) 200 μl of the 20% $MgCl_2$ solution and (B) 60 μl of the 50% $MgCl_2$ one. In Fig. 1-D the data of the reference $CdCl_2$ treated sample are also shown.

When 200 μl of 20% $MgCl_2$-solutions and even more concentrated ones are applied, the CdTe charge density is higher being over 10^{14} cm^{-3} and it extends for more than 2 μm from the junction. As the amount of the treatment solution used increases, also the carrier charge density increases. In fact Cl-based treatment promotes the intermixing between CdS and CdTe active layers at the junction and enables a recrystallization of the CdTe absorber layer. All these phenomena result in a reduction of the lattice mismatch at the p-n junction and as a consequence also a decrease in the interface defect density, which are carrier traps and act as a barrier for the current transport.

Nevertheless by considering the photovoltaic parameters of Table 2 it can be noticed that for $MgCl_2$-treatments stronger than 60 μl of 50%-concentrated solution, samples start to have lower open circuit voltage (Voc) and then lower efficiencies. This behaviour can be related to a different defect concentration of inside the active materials, which can be explained by the difference in their C-V and DLCP spectra (Fig. 1-A, B).

Since DLCP is a more selective technique for shallow defects, while by C-V it is possible to obtain information about the kinetics of carrier transport through both shallow and deep defects, from the comparison of their spectra and more precisely from their difference it can be estimated a qualitative concentration of deep defects into the material studied [5].

With low amount of solution (100 μl, 20% concentration: Fig. 1-A the device shows a low carrier concentration (in the 10^{13} cm^{-3} range) with an evident separation between DLCP and C-V. On the other hand with 200 μl of the 20% concentration solution (Fig.1-C) the charge density increases up to the 1×10^{14} cm^{-3} range but DLCP and C-V are superposed, suggesting that over a certain $MgCl_2$ quantity, the deep defects are compensated. This is also supported by the fact that for samples with $MgCl_2$ 20% concentrated solution the C-V lines are below DLCP even at 300 K, which can be explained by a compensation of the deep defects.