AGEING OF CdTe DEVICES BY COPPER DIFFUSION

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CdTe solar cells are widely used in industrial production and they currently have the lowest cost per Watt available in the market thanks to its simple and scalable technology. One of the main engineering challenges for these devices is to provide a suitable back contact for CdTe due to its high electron affinity which requires a material with a very high work function. Solar cells with copper based back contacts have shown the highest efficiencies, however it is well known that their performance reduces with time, mainly connected with diffusion of Cu through the absorber. Working conditions (i.e. light intensity, temperature and applied bias) can dramatically affect the degradation speed. In order to study the impact of the bias on the Cu diffusion, then on performance degradation, three different kinds of stress were applied on identical CdTe solar cells with Cu/Au back contact (Dark without bias, light-temperature without bias, light-temperature with bias). The degraded devices have been periodically analyzed by current-voltage, capacitance-voltage, drive level capacitance profiling and admittance spectroscopy. A detailed analysis of defect characterization and distribution has been addressed.
Keywords: Thin Films, CdTe, Degradation, Defects, Back contact.

1 INTRODUCTION

CdTe solar cells are widely used in industrial production and they currently have the lowest cost per Watt available in the market thanks to its simple and scalable technology.

Despite the industrial feasibility and the promising perspectives, for many years CdTe devices have remained in the laboratory scale and it took more than two decades to bring CdTe modules to the market. One of the main reasons for this is the difficulty in engineering a suitable back contact for CdTe due to its high electron affinity which requires a material with a very high work function.

Nowadays modules based on CdTe technology are produced with back contacts made by a wide range of materials (e.g. Sb_2Te_3, As_2Te_3, etc…)[1] ensuring high stability, but usually increasing the series resistance and consequently the interconnection losses. Usually the best performances are achieved by addition of copper in the back contact that reduces roll-over effect and enhances the absorber electrical properties. However it is well known that copper diffuse through the grain boundaries until it reaches the CdS/CdTe junction progressively shunting the cell with a consequent efficiency reduction mainly connected with Fill Factor (FF) and open circuit voltage (Voc).

According to the certification protocol IEC 61646 to estimate the performance degradation, modules are usually tested applying high temperature (85 °C) and/or irradiation, but no external load is expected. Laboratory tests often introduce biases to better understand the degradation process, which is usually connected with Cu migration from the back contact [2-4].

In our lab several CdTe solar cells with Cu/Au back contact have been prepared in the same way, and then differently stressed by means of a chamber where temperature, illumination and bias can be controlled. A set of cells were stored in dark conditions at room temperature (RT) while another was stored in the chamber in light condition (1 sun) at fixed temperature (80 °C) with no bias and another set was stored in the same chamber but shunting front and back contact.

Sets of cells have been periodically analyzed by current-voltage (J-V) characterization, capacitance-voltage (C-V), drive level capacitance profiling (DLCP) and admittance spectroscopy (AS).

2 EXPERIMENTAL

CdTe solar cells sets have been prepared with the following procedure. Front contact is made by depositing 400 nm of indium tin oxide (ITO) and a 100 nm ZnO on soda lime glass at 300 °C respectively by direct current reactive sputtering and radio frequency sputtering. Successively 400 nm CdS and 7 μm CdTe have been deposited in the same chamber by vacuum evaporation with substrate temperatures respectively of 100 °C and 340 °C at 10^{-6} mbar; $CdCl_2$ recrystallization treatment has been applied by a wet activation treatment: depositing micro-liters of $CdCl_2$-methanol saturated solution and annealing the stacks in air at 410 °C for 30 minutes; before contact deposition bromine-methanol bath was used to etch the surface in order to remove $CdCl_2$ residuals and create p^+ Te rich layer. Finally 2 nm copper and 50 nm gold were deposited by vacuum evaporation without heating the substrate but with a subsequent annealing in air at 190 °C for 20'. Such small amount of copper is the best trade-off between high efficiency and stability (copper diffusion). Bigger amount of copper would reduce the roll-over effect resulting in higher fill factor and higher efficiency, but providing a higher copper migration from the back contact.

J–V characteristics for all cells were measured by Keithley SourceMeter 2420 at RT.

DLCP, C-V and AS were measured by HP4284A LCR. Temperature was changed using a Janis cryostat with Lakeshore 325 temperature controller in a vacuum of 10^{-6} mbar and in a range of temperature between 100 K and 320 K. It is worth to note that temperatures over 320 K have been avoided not to affect the Cu diffusion from back contact during the measurements.

All kinds of measurements have been repeated at different cells lifetimes along the ageing process in order to follow the devices performance degradation.

C-V/DLCPs have been performed at different frequencies, in particular 10 kHz, 50 kHz, 100 kHz and 1

MHz, to analyze the defects response.

AS were performed in a range of frequencies between 300 Hz and 1 MHz and temperatures. Each measurement has been repeated with applied direct current bias of 0 V, -0,5 V and +0,5 V.

Three different kinds of ageing were performed at different conditions:

1. Dark, room temperature and No Bias (DNB)
2. Light, high Temperature and No Bias (LTNB)
3. Light, high Temperature and Bias (LTB)

In the first case, samples were simply stored in a drawer, in the second they were stored in a metal chamber with halogen lights and equipped with fans and a temperature controller made to maintain the temperature constant at 80 °C, and light exposure of 1000 W/m^2. In the third case cells were stored in the same chamber, in same conditions but with front and back contact shunted, current was controlled by an amperometer.

It is worth to note that 1000 W/m^2 in the ageing chamber was generated by halogen lamps calibrated by a silicon solar cell. As long as the emission spectrum of these lamps differs from the solar one, in particular in the ratio between infrared and visible wavelength, it is possible that using silicon wavelength as a reference could result in inaccuracy in light intensity exposure. However the goal of this work is to compare the effects of similar kinds of stress on devices made by the same production process, not to reproduce the modules working conditions or to extrapolate a multiplication time factor.

3 DISCUSSION

3.1 J-V Measurements.

J-V measurements at different ageing time have been performed on devices stressed as described in previous paragraph. Unfortunately it was not possible to measure all the samples at the same time, for this reason time intervals differs, however Fig. 1 shows clear difference among the stress effect on the devices.
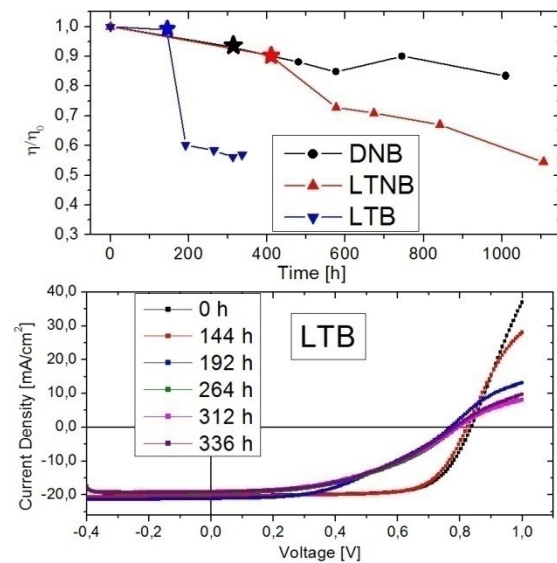

Figure 1: Top. Normalized efficiency evolution for the different kinds of stress. η_0 represents the efficiency at t=0 h, stars indicate the starting point of the stress. Bottom. Typical J-Vs of 3rd set of sample (LTB) at different ageing time.

Fig.1 top side shows the typical efficiency evolution due to the applied stress. In all cases the point replaced with a star indicates the starting point of the relative stress; pre-stress measurements were performed to check if the cell was stable, ensuring the following degradation was related only to the applied stress.

It is possible to note that for the samples stored in DNB conditions the degradation trend continues after the star with no changes. It is also interesting to note that after more or less 600 h (hour) efficiency peak appears. This peak was registered on 9 cells over 10 that have been measured and it seems to be driven by similar peak in FF, Jsc and Voc don't present it. DNB J-V characteristics (not shown here for space reason) present a progressive reduction in FF and in roll-over, but no remarkable changes in Voc and Jsc. A possible explanation is a migration of copper from back-contact increasing the back diode barrier height and in the same time shunting the cell. After around 1000 h efficiency goes from the initial 13.5% to 11.3%, with a performance loss of 16%.

Cells aged in LTNB conditions show a dramatic efficiency decrease after first stress application and a kind of stabilization of the degradation trend that brings to a loss of 45% efficiency at the end of the ageing.

In the last case (LTB), the shunt between front and back contact allowed a continuous current flow close to Jsc value. This stress results to affect much more the device performance achieving the whole LTNB degradation after only 50 h instead of 1100 h.

In the bottom of Fig.1 the J-Vs of typical LTB sample are shown. Pre-stress curves (black squares and red circles) indicate very slow degradation with slight performance loss mainly due to Voc reduction. After the stress, degradation is dominated by FF that decreases of -38% (from almost 71% to 44%) while Voc decreases just of -6% (from 824 to 775 mV) and Jsc increases of +3,5%. Despite some fluctuations in parameters, performance remains more or less stable after the first stress, for this reason ageing of these samples was stopped after only 360 h.

3.2 DLCP and C-V Measurements

DLCP and C-V measures were performed to investigate the suspected migration of copper along devices. Measures have been repeated at different ageing time but, for reason of space and clarity, only the most interesting results are presented.
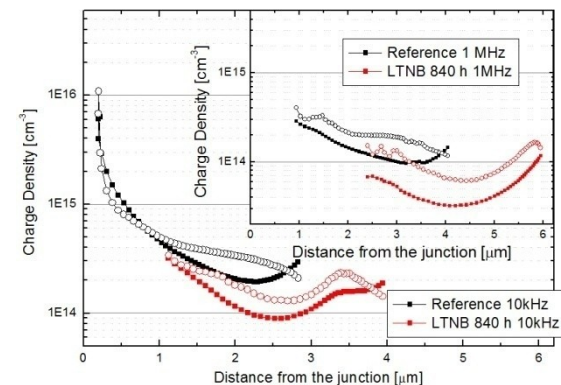

Figure 2: Comparisons between DLCP (full dots) and C-V (open dots) profiles of LTNB sample at 300 K and 10 kHz. In the inset a similar comparison at 1 MHz.

DLCP and C-V profiles analysis yields the net space charge concentration and its distribution along the <x> direction of the devices. DLCPs indicate the concentration of defects lying close to the valence band (shallow defects) at certain temperature and frequency conditions. On the other hand C-V profiles provide all active defects density both shallow and deep (lying closer to the mid-gap energy). The difference between the two profiles at certain voltage results in deep defects concentration. In these analyses increasing frequency means to inhibit slow defects that contribute to the measured charge value, so only fast defects are revealed. Similar inhibition effects can be performed reducing the temperature of the samples. As long as temperature decreases ionized defects concentration decreases as much as their energy is closer to the mid-gap energy.

Fig.2 shows profiles obtained at 300 K and 10 kHz (1 MHz in the inset) of a sample aged in LTNB condition. Black symbols profiles represent the reference measured in pre-stress time, red symbols profiles show the effect of the stress. After 840 h in LTNB conditions both defects concentrations are sensibly lower than the reference. For example at 2 μm, shallow defect concentration was around $2 \cdot 10^{14}$ before the stress and $1 \cdot 10^{14}$ after the stress. Deep defects concentration decreases from $1,3 \cdot 10^{14}$ to $5 \cdot 10^{13}$. In the proximity of the junction (between 0 and 1μm) in both cases deep defects are not present while shallow defects concentrations dramatically increase achieving similar values.

In the inset of Fig.2 1 MHz profiles are shown. If we compare the ageing profiles with the reference is possible to see that deep defects concentration does not change after ageing (e.g. at 3μm it is constant around $7 \cdot 10^{13}$), and shallow defects concentration decreases from $1 \cdot 10^{14}$ to $5 \cdot 10^{13}$. LTNB ageing reduces both shallow and deep defects densities away from the junction. Moreover fast shallow defects involved in ageing degradation represent 50% of total amount, but only slow deep defects density seem to be changed by this kind of stress.
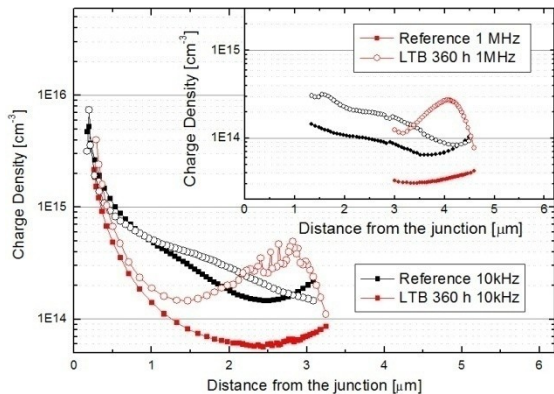
$2,5$ μm it is $1,5 \cdot 10^{14}$ for the reference profile and around $6 \cdot 10^{13}$ after 360 h. On the other hand deep defects concentration increase after LTB stress (from $1 \cdot 10^{14}$ to $2 \cdot 10^{14}$) while it was reduced by LTNB.

In the inset of Fig.3 the same comparison is presented at 1 MHz. Also at high frequency shallow defects density decreases and deep defects concentration increases (e.g. at 3,5 μm changes from $5 \cdot 10^{13}$ to $1,4 \cdot 10^{14}$). A possible conclusion is that most of deep defects generated by this stress are fast. Another possible consideration is about the influence of back-contact capacitance on the measurement: if it increases enough to be comparable with the main junction capacitance they can be considered as two capacitors in series, this reduces the equivalent circuit capacitance that is no longer connected with defects concentration in the device. LTB profiles at 1 MHz extend from 3 μm up to 5 μm while in LTNB extend from 2,5 μm to 6 μm. This reduction is due to the whole space charge density (right side) and back-contact capacitance (left side). This means that the LTB back contact capacitance is more pronounced with respect to the LTNB. Furthermore this difference is appreciable more at 1 MHz than at 10 kHz. From the C-V curves (not shown here) the LTB back-contact at 1 MHz seems to behave in anomalous way and this is the most probable reason for such short profiles.

It is worth to note that reference profile of this sample is very similar to the one shown in Fig.2, this ensure that the reported differences are related only with the different stresses.

A similar comparison (not shown here) was done for samples aged in DNB conditions for 480 h. It brought out that reference and stressed sample profiles perfectly coincide either at 10 kHz or 1 MHz. So variation of shallow and deep defects densities was not registered. Anyway DNB ageing produces some degradation of performance that can be also related with some variation of doping profiles, but they are probably too small to be appreciated by this technique.
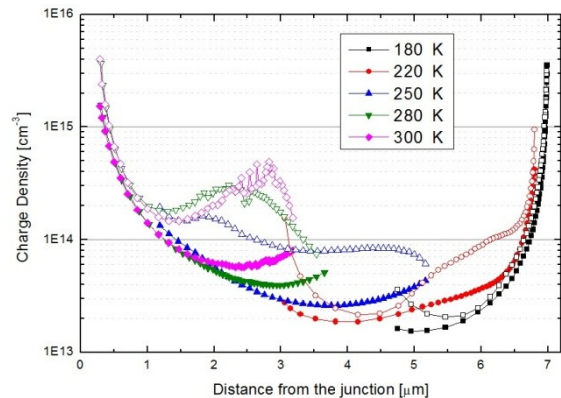

Figure 3: Comparisons between DLCP (full symbols) and C-V (open symbols) profiles of LTB sample at 300 K and 10 kHz. In the inset a similar comparison repeated at 1 MHz.

Figure 4: Comparisons between DLCP (full symbols) and C-V (open symbols) profiles of LTB sample at 10 kHz and in a range of temperature from 180 K to 300 K.

Fig.3 shows profiles measured at 300 K and 10 kHz (1 MHz in the inset) of a sample aged in LTB condition for 360 h. Profiles shown in Fig.3 and in Fig.2 in the junction region are very similar, even if the increment of shallow defects and the reduction of deep defect appears to be more abrupt in case of LTB. The reduction of shallow defects density away from the junction has the same magnitude than in LTNB case, so for example at

In Fig.4 the evolution of shallow and deep defects profiles in temperature range between 180 K and 300 K for LTB sample is shown. From 180 K to 220 K both shallow and deep defects densities increase sensibly. From 220 K up to 300 K shallow defects concentration increases gradually, but from 250 K to 280 K deep defects concentration increases from $6 \cdot 10^{13}$ to $2,2 \cdot 10^{14}$. Moreover close to the back contact, the profile at 220 K

(red curve) is similar to the one reported by [2]. This information together with AS results can help to identify the deep defects responsible of the performance degradation.

3.3 AS Measurements

Admittance Spectroscopy is performed measuring the device capacitance sweeping the frequency. If a dominant defect is present when its activation frequency is overcome the capacitance abruptly drops. From the defect activation frequency evolution on temperature it is possible to extract the defect activation energy (E_a) and its capture cross section (σ_a). In cells with high performance like reference cells mentioned in previous paragraphs, it is usually possible to identify many defects active at different temperatures. Unfortunately when the contact degrades high frequency measurements become noisy preventing a correct extraction of the defect parameters especially at low temperature. Table I summarizes the parameters that have been extracted.

Table I: Activation energy and cross capture section

	E_a [meV]	Error [meV]	σ_a [cm^{-2}]	Defect
Reference	150	1	$1,70 \times 10^{-14}$	A1
	460	14	$1,20 \times 10^{-12}$	A2
	527	11	$1,00 \times 10^{-11}$	A3
LTNB	74	3	$3,57 \times 10^{-18}$	B1
	96	3	$2,64 \times 10^{-17}$	B2
	500	17	$3,75 \times 10^{-12}$	B3
	636	2	$8,51 \times 10^{-10}$	B4
LTB	379	2	$9,83 \times 10^{-15}$	C1
	421	8	$3,38 \times 10^{-13}$	C2

For reference we address the defects extracted before applying any stress. We have reported similar values in previous works [5]. The A1 is typically connected V_{Cd} V_{Te} and (V_{Cd}-Cl_{Te}) [6][7], A2 not esaly attributable and A3 probably connected with Te$^-$ or Te^{2-}[6]. In LTNB are present shallow defects never reported before in CdTe solar cells (B1 and B2), and deep defects B3 and B4, the first probably not connected with Cu and the second probably connected with CdCl$_2$ [6]. In the LTB sample extraction of shallow defects at low temperature was too uncertain, but deep defects were clearly extracted. With respect to C2, also observed by Beach et al. [6], we avoid any identification because there is not evident match with reported defects in literature, even if seems to be quite similar to A2. On the other hand C1 has been reported by [6][7] and identified like Cu$_{Cd}^-$, so we can suppose that the increased deep defects concentration revealed by C-V and DLCP can be connected with the appearance of this peak in the AS which was not visible in the other types of samples.

4 CONCLUSIONS

Three set of cells have been prepared by the same process with the same characteristics. The cells were aged applying different stresses (Dark No Bias, Light high Temperature No Bias, Light high Temperature and Bias) in order to study copper diffusion from the back contact through the device.

The J-V characteristics show very different effects of the three ageing stress on the devices performance. The DNB yields a degradation of about 16 % in 1000 h. It must be noted that from 600 to 1000 h the efficiency doesn't decrease so much. In this case it is possible to conclude that after the first loss the devices stabilize. In case of LTNB the stress application causes a quick reduction of performances followed by a slower degradation that results in overall loss of 45% in performance. In the last case (LTB) a similar behavior was registered, the stress application yields an even more dramatic drop of the efficiencies (45% in only 360 h) followed by similar stabilization.

J-V characteristics analysis brings out that all degradations are mainly driven by FF losses.

DLCP and C-V profiles have shown evident differences in three cases. After 480 h DNB shows identical profiles, whereas LTNB a sensible reduction in shallow and deep defects concentration, probably indicating compensation. On the other hand in LTB case the reduction of shallow defects is confirmed, but deep defects concentration sensibly increases along the absorber.

In case of LTNB typical CdTe deep defects were registered by AS. Shallow defects, not present in the reference sample, were registered but not identified, because, to our knowledge, never reported in literature.

In LTB samples the shallow defects extraction was not possible probably due to the strong performance degradation. However two kinds of deep defects were registered. One of these (C2) is very similar to a defect present in the reference (A2). The other defect (C1) was revealed only in LTB and is probably responsible of the increased deep defects concentration carried out by DLCP and C-V.

Taking into account that LTB provides the strongest degradation, opposite of what observed by [2], we can conclude that the models proposed are not suitable for our samples. A possible explanation is that copper, under DNB conditions, is moved only by concentration gradient, diffusing slowly and with no appreciable changes in defects concentration and position. Under light and temperature stimulation Cu massively diffuses compensating the absorber. If also an electron flow is applied, Cu atoms migrate with increased energy, generating deep defects like Cu$_{Cd}^-$ that result in enhanced recombination, excluding the presence of positively ionized copper atoms as it was proposed by Corwine et al. [2]. This could be explained by different etching, providing a different intermixing between copper and CdTe.

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