STUDY OF THE EFFECT OF ABSORBER ETCHING ON THE BACK CONTACT PERFORMANCE OF CDTE SOLAR CELLS

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ABSTRACT: The application of copper in the CdTe back contact is believed to be crucial to form an ohmic contact with CdTe. On the other hand it has actually shown other beneficial effects such as increasing the carriers concentration, indeed the highest conversion efficiencies have been obtained only with copper insertion. However it is not clear if this is due to a compensation reduction or to a formation of new defects in bulk CdTe. Moreover, the role of the etching process is also very important, it is believed that a tellurium rich layer is formed which might react with copper forming Cu_xTe. We have prepared CdTe devices with Cu/Au back contact on differently etched CdTe surface and tested them by applying thermal, luminous and electrical stresses. The devices and their degradation effects are studied by current-voltage, capacitance voltage, drive level capacitance profiling and admittance spectroscopy characterization techniques and the etching effect is analyzed by Raman measurements.

Keywords: CdTe, Back Contact, Etching

1 INTRODUCTION

CdTe is a simple, stoichiometric and robust material that has shown a remarkable market success in thin film solar cells. It is well known that deposition of both CdS and CdTe materials can be made with a very large number of techniques and with good working conversion efficiency; indeed the scalability of the fabrication process is probably the most interesting aspect of this technology.

However some aspects have been limiting the possibility to scale up the production, most important it is the stability and the impact on the efficiency of the back contact.

It is very well known that high efficiency devices have been obtained by introducing copper into the back contact sandwich, moreover a specific etching of the CdTe surface is considered necessary in order to produce a rich tellurium layer that would not only give place to a p^+ layer but also be able to react with copper forming Cu_xTe and generating an ohmic contact [1]. However many contradictory results have been presented before: high efficiency devices have been obtained also without surface etching, claiming that only a shallow cleaning of the surface would be necessary [2].

In this paper we present a comprehensive study of the effects of bromine-methanol etching (Br-MeOH) with copper/gold back contact on the solar devices. The etching processes have been applied with different application time and the devices have been compared with the ones made without etching. Raman and Grazing Incident X-Ray diffraction (GIXRD) spectroscopy and Atomic Force Microscopy (AFM) on the etched and non-etched CdTe have been used to study the structural changes of the surface. These data are compared with the study of current-voltage (JV), capacitance-voltage (CV), drive level capacitance profiling (DLCP) performed on the finished devices and defects are addressed.

2 EXPERIMENTAL

CdTe solar cells, in our laboratory, are usually prepared as follows. On a common soda lime glass, 400 nm of indium tin oxide (ITO) and a 100nm ZnO are deposited at 300°C respectively by direct current reactive sputtering and radio frequency sputtering.

Successively around 150nm CdS and 6 um CdTe are deposited in the same chamber by vacuum evaporation with substrate temperatures respectively of 100°C and 340°C at 10^{-6} mbar. Our activation treatment consists of a wet $CdCl_2$ annealing: we put drops (micro-liters) of $CdCl_2$-methanol saturated solution (previously prepared) and then anneal the layers in air typically at 410 °C for 30 minutes [3]. In this work we will also present GIXRD patterns of CdTe/Cu/Au stacks with absorbers activated at 395°C and they will be compared with the ones of the standard process (activation at 410°C). Prior to the deposition of 2nm of copper and 50nm of gold (by vacuum evaporation) a bromine-methanol etching of the CdTe surface is applied. Finally annealing in air at 190 °C for 20 minutes is performed.

The above mentioned copper amount is the result of a thorough optimization, which is a trade-off between performance, especially in terms of roll-over, and stability, due to unwanted copper diffusion in to the junction of the device [4].

Current-voltage (JV) characteristics were performed with a Keithley SourceMeter 2420 at room temperature with an irradiation of $1000 W/m^2$. On the other hand the aging of the cells have been provided by a specific metal box, where a rack of halogen lamps and a temperature system control allows to leave the cells under one sun and 80°C, accelerating aging time.

Different solar cells have been prepared with same layers but with a different preparation of the back contact, where the CdTe surface was either not etched or etched with different etching times. The surface preparation was also combined with different copper quantities in order to analyze how copper would react with a possible different amount of tellurium rich layer. In table I, the most significant combinations taken into account with best efficiencies are shown. Etching time was changed from 5 up to 40 seconds; 50 nm of gold were deposited in any case.

Table I: Summary of different back contact configurations

	Etch. time s	Cu nm	V_{oc} mV	J_{sc} mA/cm^2	F.F %	η %
1	0	2nm	802	23	65,6	12,1
2	0	4nm	824	24.2	68,8	13,7
3	5	2nm	824	23.5	65,8	12,74
4	40	2nm	838	22.8	72	13,75

Similar electrical values with high efficiencies (between 13 and 14%) for our standard solar cells also with no etching of the surface but with 4 nm of copper have been measured, as shown in Table I: even without surface etching it is possible to fabricate a high performing device. On the other hand with only 2nm of copper and no etching, as well as with only 5s etching time the efficiency drops, suggesting that bromine-methanol time etching should be inversely proportional to the amount of copper.

3 ANALYSIS OF EFFECTS OF THE BR-MEOH ETCHING

3.1 Raman analysis

In order to study the etching effect on the structural properties of the CdTe surface, room-temperature micro-Raman spectra were recorded in backscattering geometry by exciting the samples with 514.5 nm line of a mixed Ar–Kr ion gas laser, using a triple-monochromator coupled to a nitrogen cooled CCD detector (1024Å~256 pixels). Not etched, 5s etched and 40s etched CdTe surfaces have been analyzed (see Fig. 1) and Raman measurements clearly confirm that bromine-methanol etching process develops a tellurium rich layer, as shown in figure 1, which is not present in the as deposited case. This shows that even without the generation of a Te rich layer it is possible to perform high efficiency. Moreover the measurements also demonstrate that the quantity and quality of tellurium do not depend on the etching procedure, spectra taken at two different positions show alternatively higher peaks for the 5s etching in one case and for the 40s etching in the second case.

3.2 CV and DLCP analysis

In order to investigate if etching of the surface would also influence the concentration and the quality of the defects, devices prepared with the different back contact conditions mentioned above have been studied by means of CV and DLCP at room temperature and different frequencies, in order to address the shallow and deep defects for each case [5].

Drive level capacitance profiling (DLCP) and capacitance-voltage (CV) study was made with a HP4284A LCR at room temperature.

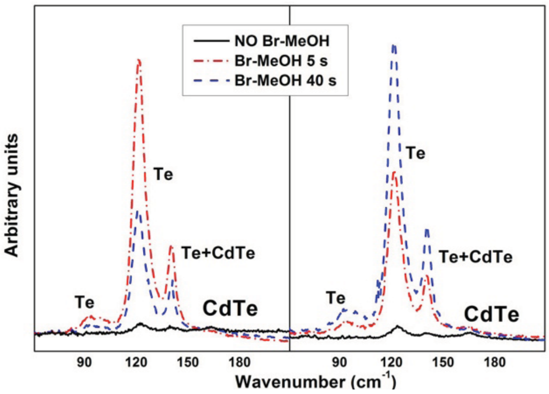

Figure 1: Raman patterns on CdTe surface with no etching (black solid line), with Br-MeOH 5s etching (red, dash dot line) and with Br-MeOH 40s (blue, dash line)

In Fig. 2, we compare devices made with not etched and 40s etched CdTe surface at a frequency of 100kHz and 10kHz (see inset). The DLCP lines show that the etching affects the net carriers concentration by increasing it.

This macroscopic information can be analyzed if we look carefully at the behavior of the curves. The difference between DLCP and CV lines, which gives the qualitative information on the amount of deep defects, is different for the two cases. The not etched device shows a uniform distribution of these defects all along the CdTe depth from the bulk to the back contact, on the other hand in the 40s etched case the deep defects are concentrated in a smaller area far from the back contact region. For the higher frequency case (100kHz) the CV characteristic of the etched-CdTe surface device seems to have a sharper peak, suggesting that some of the defects are froze out while for the not etched case the behavior is the same as before. From this we can observe that probably we are dealing with different type of defects for the two devices. In the next chapters an introductive analysis of the defects by admittance spectroscopy (AS) will be presented, in order to identify their nature.

Indeed, we do not only see different defects concentrations but also, more important, a different nature of some defects between the two samples.

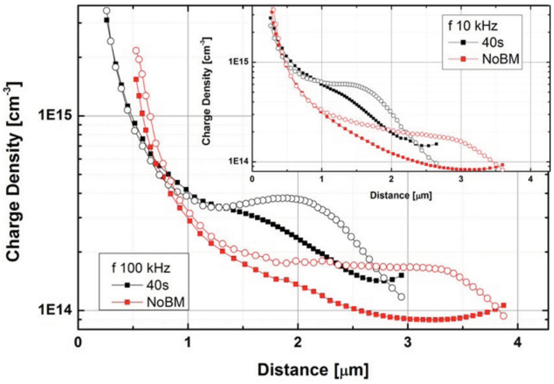

Figure 2: DLCP (full dots) and CV (empty dots) analysis of devices without CdTe surface etching (red line) and with 40sec CdTe surface etching (black) at 100 and 10 kHz (inset)

3.3 GIXRD analysis

The GIXRD measurements have been performed at IMEM (CNR) on a high-resolution diffractometer provided with a Goebel monochromator selecting the CuKα lines from a sealed x-ray tube with Cu anode. During the 2theta scan the grazing angle on the sample surface was fixed to 0.5° with a 2θ resolution of 0.05° obtained by a Soller slit in front of the detector.

Fig. 3 shows the GIXRD peaks obtained on the surface of finished devices with CdTe activated at 410 °C (top) and 395°C (bottom) and not etched, 5 s and 40 s Br-MeOH etched surfaces. Together with the expected CdTe and Au peaks, several peaks attributable to different compounds are observed. For the 410°C activated absorber, CuTe peaks are preferred in the etched samples while Cu_2Te is strongly present in the not etched case. On the other hand if a different activation treatment is applied, with an activation temperature of 395 °C, the Cu_2Te peaks are predominant also for the 5s Br-MeOH case.

This shows that etching, as also suggested by the CV and DLCP measurements, do not only remove the $CdCl_2$ residues and generates a Te-rich layer but effectively gives place to a different structure, which is also dependent on the previous preparation steps (such as process temperature), that influences the electrical properties of the cells.

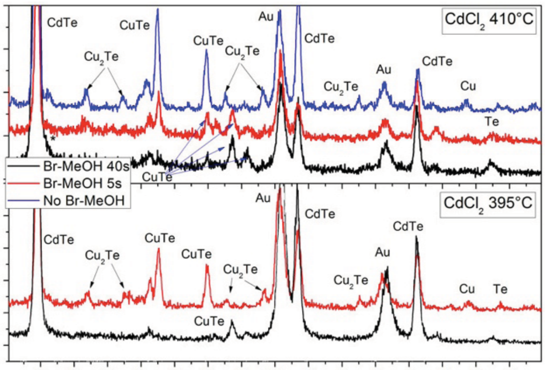

Figure 3: GIXRD diffraction patterns of activated CdTe at 410 °C (top) and 395°C (bottom) for not etched (blue line), 5s etched (red line) and 40s etched (black line) surface in Br-MeOH

4 AGING BEHAVIOUR

4.1 Accelerated lifetime stability tests

As mentioned above the stability of the finished devices with different etching processes have been tested on an accelerated lifetime box, the devices have been subsequently measured at different aging steps. They have been tested in open circuit condition (V_{oc}) but some of them were put in a closed electric circuit in order to age them with forward current flowing (J_{sc}).

All the devices are degrading, as expected from a copper/gold back contact, but definitely not in the same way. As a matter of fact, solar cells working in Jsc-mode are more stable than the ones in open circuit condition. This phenomenon has been already reported [6] and can be explained if Cu is taken as a positive ion. Copper diffusion inside the CdTe/CdS structure would than depend on the junction internal field that, in turn, depends on the fact that the cell is driven by an external bias or is illuminated by one or more suns.

In Fig. 4 the degradation, in terms of fraction of initial efficiency, for devices left in the previously described black box is pictured.

The stability of the device with not etched CdTe is poor compared to the remarkable stability of the 40s etched case. Even with a less amount of copper such as 2 nm (right-bottom in the picture), after 900 hours at one sun and 80°C the efficiency is less than 40% of the initial efficiency, while after more than 1000 hours at the same conditions the 40s etching case gives a device with still 80% of the initial efficiency.

Devices made with CdTe etched for 5s in Br-MeOH are slightly less stable, dropping to less than 70% of their initial efficiencies after more than 1000 hours in accelerated testing conditions.

These results show how the etching is influencing the back contact formation, as also observed from the GXRD data. The 40s etching provides a CdTe surface that is able to form CuTe instead of Cu_2Te (which is an unstable compound), providing solar cells with a superior stability under short circuit conditions. In this case we are able to produce a device that keeps its 80% of the initial efficiency, as generally promised from the producers' warranty, even with a Cu/Au standard back contact.

With 5 seconds etching, some Cu_2Te (see Fig.3) is generated, especially in the 395 °C activation treatment, and this results in a lower performance in stability of the devices.

When no etching is applied we can observe a peak of pure Cu and an evident presence of Cu_2Te (see Fig.3), which explains the low stability shown in Fig. 4.

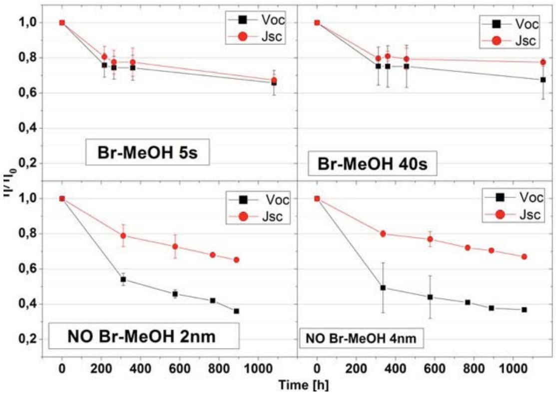

Figure 4: Relative efficiency (with error bars) after accelerated lifetime stability test for devices with etched (top, 5s left and 40s right) and not etched (bottom, 2nm Cu left and 4 nm Cu right) CdTe surface up to 1000 hours

4.2 CV and DLCP analysis of degraded devices

Analogously to what has been shown in section 3.2, an analysis of CV and DLCP behavior was applied to degraded device with 40s Br-MeOH etching and compared with the initial behavior.

The choice for this sample was given by its good performance after the aging, which would not invalidate the measurements as in the case of very strong degraded devices.

In Fig. 5 the behavior of the solar cell before the aging is shown. A net carrier concentration of nearly 10^{15} cm^{-3} is registered, which after 1500 hours in the "black box" is reduced by an order of magnitude.

However most important is the difference between DLCP and CV before and after aging. In the last case the DLCP and CV lines have almost one order of magnitude difference especially at 10MHz and they are both much lower than the corresponding ones of the not aged device. However this cannot be explained by an absolute reduction of the defects by aging, but more likely by a compensation of the shallow defects. Given by a formation of shallow donors, this is also supported by the fact that compensation is much lower for the deep defects as shown in the inset of Fig. 5. Moreover the freeze out of the shallow defects at 1 MHz is observed.

Another effect of the aging shown in Fig. 5 is the homogeneous distribution of the defects after the degradation while before the curves we have a peak at around 1,5 microns, this suggests the formation during the aging of defects with different nature, that would be identified by admittance spectroscopy.

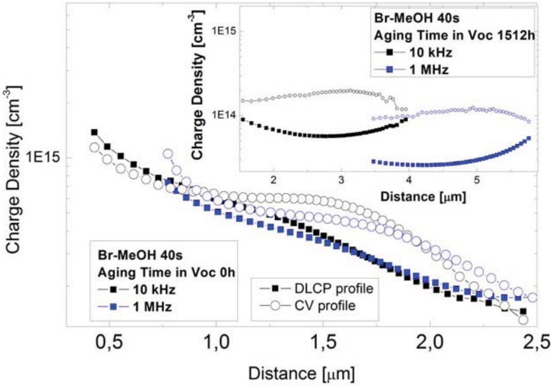

Figure 5: DLCP (full dots) and CV (open dots) of devices with 40s Br-MeOH etched surface before and after (inset) aging a 10kHz (black) and 1 MHz (blue)

A preliminary admittance spectroscopy study has been performed which identifies the presence of Cu_{Cd} defect which is connected to deep defects concentration for devices with not etched CdTe. But, more important, the formation of donor shallow defects after aging for devices with 40s etched CdTe have been observed. More detailed analysis will be presented in a future work.

5 CONCLUSIONS

Low temperature CdTe devices deposited by vacuum evaporation with efficiencies between 12 and 14% have been prepared with different CdTe etching procedures and different copper amounts. High efficiencies were obtained also by not etching the surface.

Raman measurements show that there is no difference in tellurium amount when a Br-MeOH etching is applied, irrespective of the etching time. However a very different structure of the back contact is observed: with 40s and 5s etching a CuTe surface is formed while with no etching Cu_2Te is also present.

This last one explains the stronger degradation of the cells; only the devices with etched CdTe show a relative stability, in case of 40sec etching the device is more bias dependent showing a remarkable stability in Jsc conditions. The comparison of CV and DCLP measurements of not etched and 40s etched devices show a different behavior where more deep defects are homogeneously distributed in case of not etched devices. After aging strong formation of deep defects and their wider distribution all along the CdTe is registered, together with a reduction of net carrier density of one order of magnitude. These phenomena explain the final lower efficiency after 1000 working hours at one sun and 80°C.

Finally we can conclude that Br-MeOH etching is not only cleaning the surface from $CdCl_2$ residues and not simply providing a Te-rich layer but especially it is changing the structural properties of the back contact (when copper is applied), provides different nature of defects in the CdTe bulk and tunes the stability of the device.

By tuning the CdTe surface etching is possible to control the stability of the back contact since the nature of intermediate layers is changed. With more investigations and especially further optimization a stable Cu-Au back contact would be an affordable result.

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