

A study of the back contacts on CdTe/CdS solar cells

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Abstract

Conventional back contacts on CdTe/CdS solar cells are commonly made with Cu/Au or Cu/graphite. Often the contact limits the solar cells efficiency and the performance degrades because of Cu diffusion to the junction. In order to get stable and ‘non-rectifying’ back contacts Sb has been applied. Pre-deposition etching treatments, post-deposition annealing, influence of Sb layer thickness and stability issues have been studied. Different etchants not only clean the CdTe surface but they also produce a conducting Te layer on the grain boundaries. Using a mixture of nitric and phosphoric acid and Sb/Au as a back contact, 12.5% efficiency cells are obtained. The stability of solar cells depends on the etching solution. Stability tests under continues 1 sun illumination suggest that under optimum condition stable cells with Sb/Au contact can be developed. A comparative analysis of the photovoltaic properties of solar cells with different back contacts will be presented. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Development of a stable and efficient back contact is essential for the long-term stability of CdTe/CdS solar cells. CdTe has a high electron affinity and therefore a high workfunction metal is required to form a good ohmic contact on p-type CdTe. Most metals don't have high enough workfunctions. Thus, back contacts on CdTe/CdS solar cells often show a non-ohmic behavior in their I - V characteristics which is usually attributed to a Schottky barrier at the back contact. This Schottky barrier acts as a diode reverse biased to the CdTe/CdS junction diode and increases the contact resistance, thereby reducing the solar cell performance [1,2].

An approach to overcome this problem is lowering the barrier by introducing an intermediate degenerated semiconductor, which increases the conductivity and creates a tunneling barrier. For this purpose the CdTe surface is etched to produce a Te rich surface [3,4]. The Te rich surface layer has an increased conductivity and is p⁺-type. Different back contact materials have been investigated so far, the most commonly used are Cu/Au [4,5], Cu/graphite [6], Cu doped ZnTe [7,8] Cu/Mo [9] or just Au [2].

Generally, efficient back contacts are obtained by applying a thin layer of Cu (60 Å) or a graphite paste mixed with Cu on the Te rich surface. After an annealing process an

intermixed Cu_xTe degenerated semiconductor layer is formed and Cu diffuses into the CdTe bulk material, where it acts as an acceptor-like dopant. The metallization is usually done with Au. The problem with Cu based back contacts is the Cu diffusion along the grain boundaries and across the junction. The cell performance, i.e. mainly efficiency and fill factor, degrades as a result of the shunting effects. Therefore, to obtain a stable CdTe/CdS solar cell it is highly desirable to avoid any Cu in the back contact. Romeo et al. [10], have demonstrated that RF-sputtered Sb₂Te₃ is a suitable back contact material. We have substituted Cu/Au with Sb/Au on CdTe in order to create an intermixed Sb₂Te₃ buffer layer on the etched CdTe surfaces.

2. Experimental and results

CdTe/CdS deposited by close space sublimation (CSS) on TCO coated soda lime glass was used for the development of Sb/Au back contacts. First, the CdTe surface was etched to clean the surface contaminations and produce a Te rich surface. In the next step a Sb/Au bilayer was evaporated without breaking the vacuum. For reference purpose, solar cells with Cu/Au back contacts were also fabricated. The stability was tested with a light soaking setup that keeps the cells constantly at an irradiation of about 1 sun (i.e. 1000 W/m² with a halogen lamp) at an operating temperature of 60°C and open circuit conditions. The cells were not encapsulated and the back contacts were unprotected.

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Table 1

Constitution of the solutions to etch CdTe layers (given in volume fractions)

Solution	Component 1	Component 2	Component 3
BrMeOH	1 Br	200 CH ₃ OH	
NP1	1 HNO ₃ (65%)	79 H ₃ PO ₄ (85%)	29 H ₂ O
NP2	1 HNO ₃ (100%)	85 H ₃ PO ₄ (85%)	33 H ₂ O

2.1. Etching of CdTe layers

Before the growth of a back contact on the CdTe layer an etching step is needed. We have investigated three different etching solutions. The compositions of the solutions are given in Table 1.

All solutions are reactive and dissolve the CdTe layer within a few minutes. In the NP solutions the nitric acid is responsible for the differential removal of Cd from the CdTe surface. The concentration of nitric acid in NP2 is 34% higher than in NP1, therefore, the NP2 etch is the most aggressive to produce an elemental Te layer in a short time (10 s after dipping).

The influence of the etching time on the CdTe surface and the cell parameters was studied in detail. The etching time was measured from the moment of dipping the cells into the etching solution. Optimum etching times for the NP1 and NP2 solutions are 60 and 10 s, respectively as shown in Fig. 1. The BrMeOH solution is a mild etchant and the influence of the etching time on the cell efficiency is not so pronounced, i.e. short etching times are sufficient for good efficiency. The average efficiencies of NP2 etched cells are higher than the efficiencies of NP1 or BrMeOH etched solar cells. A maximum efficiency of 12.5% ($V_{oc} = 780$ mV, $J_{sc} = 28$ mA/cm², $FF = 57%$) was obtained for a NP2 etched CdTe layer (the measurements were carried out with a halogen lamp calibrated to 1000 W/m² against a silicon reference solar cell).

The 4-probe measurements of the sheet resistance of the etched CdTe surface (Table 2) prove that the etching

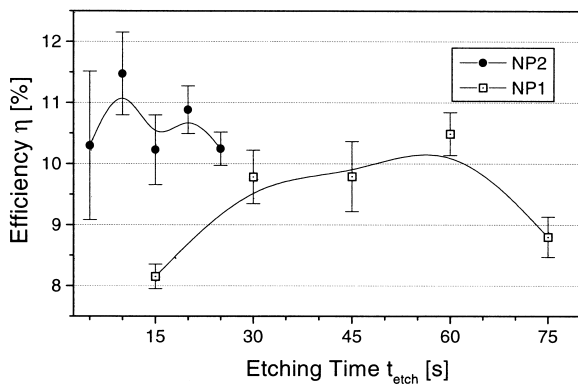


Fig. 1. Efficiencies of NP etched cells versus etching time. The back contacts were made with a 150 Å thick Sb layer. The cell area was 12.5 mm². The errors were derived by the standard deviation of many measured cells.

Table 2

Sheet resistance of the NP1 etched Te rich CdTe surfaces versus etching time

Etching time	15 s	30 s	45 s	60 s
Sheet resistance	>1/2 MΩ/□	>1/4 MΩ/□	72 kΩ/□	31 kΩ/□

produces a Te rich surface with higher conductivity. The sheet resistance of non-etched CdTe is very high but it decreases with the extra Te produced from the etching solution. A sheet resistance of 53 kΩ/□ was measured for a 12 s NP2 etched layer.

For the BrMeOH etched layers the sheet resistance was too high to measure. These values are also in agreement with the observations of earlier publications [3].

The formation of the Te layer was studied with X-ray diffraction (XRD) measurements. As shown in Fig. 2, the (1̄121) XRD peak of hexagonal Te is increasing with the etching time. The influence of the etching on the morphology of the layer and grain boundaries was observed with a scanning electron microscope (SEM). The SEM image in Fig. 3, show that the NP solutions strongly etch the surface and grain boundaries. Before etching, the surface is rather rough and the grains are dense (Fig. 3a). After etching, the grain boundaries are broadened and clearly revealed while the surface gets more smooth and polished (Fig. 3b,c). It is expected that the Te layer is not only formed on the CdTe surface but also along the grain boundaries and it provides a conductive link between grains.

The etching of grain boundaries and surface is not so strong with the BrMeOH solution. Fig. 3d shows the BrMeOH etched surface. The SEM contrasts are better when the surfaces are conductive otherwise the 'charging' effect blurs the image. Therefore, the image of surfaces with less Te look more diffuse and unfocused. The better SEM contrast of the NP etched layers also indicates the formation of a conducting Te surface layer.

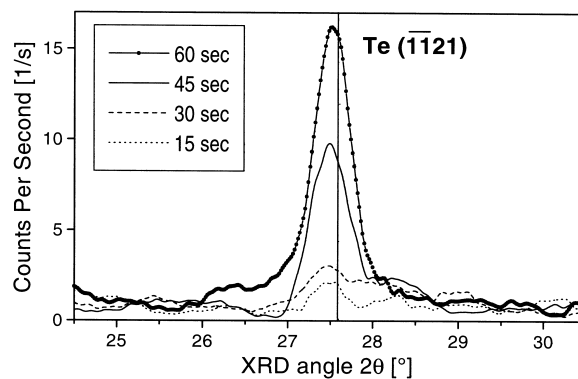


Fig. 2. XRD pattern of the CdTe layer. The Te (1̄121) peak indicates the production of an elemental Te layer at the CdTe surface with etching time.

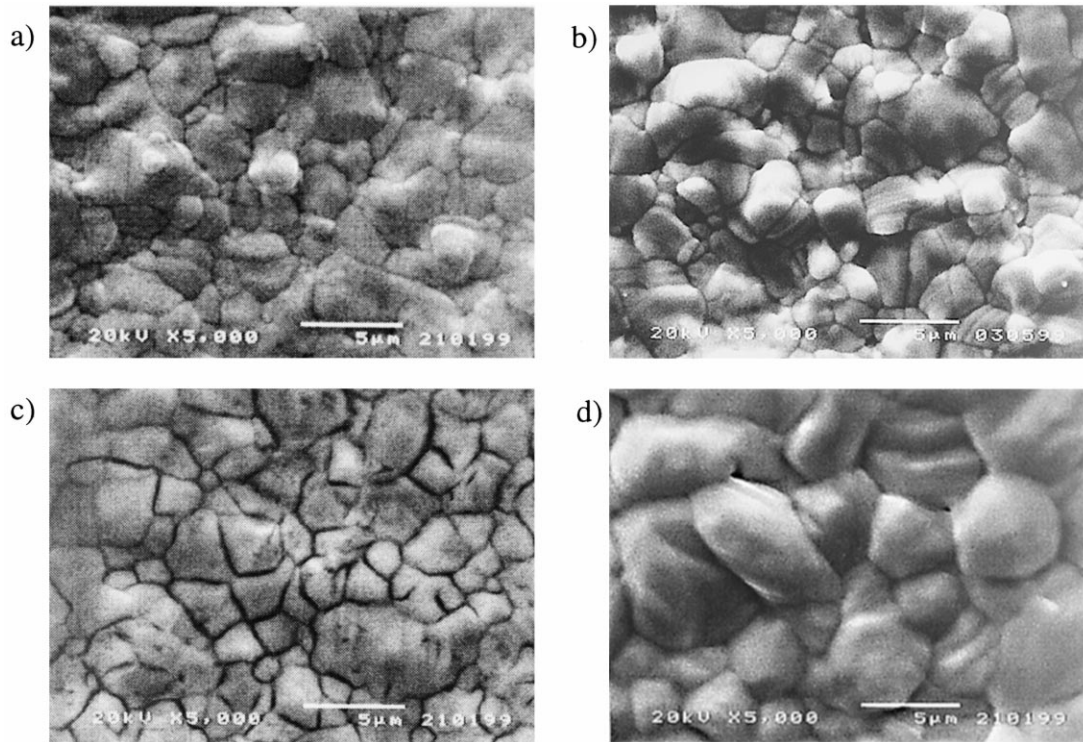


Fig. 3. Scanning electron microscope images from the etched CdTe surfaces: (a) before etching, (b) 30 s etched with NP1, (c) 25 s etched with NP2, (d) 6 s etched with BrMeOH. Image (c) shows broad grain boundaries and a rather smooth surface compared to (a), (b) and (d).

3. Solar cell performance

3.1. Annealing and stability

Photovoltaic properties of the solar cells with conventional Cu/Au and new Sb/Au contacts were compared. For the standard Cu/Au back contact and BrMeOH etched CdTe a post-deposition annealing is mandatory for high efficiencies (Fig. 4). As a result of this optimum treatment a Cu_xTe layer is formed. In addition, Cu diffuses into the bulk of the absorber layer, where it acts as an acceptor and increases the carrier density. Through this intermixing and doping effects,

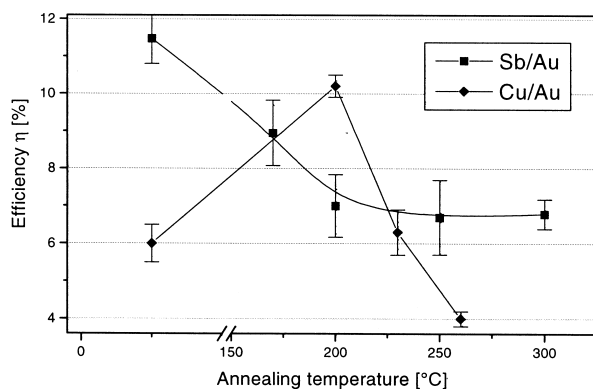


Fig. 4. Effect of annealing on the efficiency of solar cells with Sb/Au (NP2 etched) and Cu/Au (BrMeOH etched) contacts. An optimum annealing of the Cu/Au back contact is essential to obtain a good cell.

the effective barrier of the back contact is lowered and the roll over in the I - V characteristics usually observed before annealing disappears afterwards. Our measurements show that the annealing is not needed for the NP etched cells, neither for Sb/Au nor for Cu/Au back contacts. The cell parameters such as V_{oc} , I_{sc} and efficiency are already high and they degrade after annealing (compare in Fig. 4). For NP2 etched solar cells the efficiency decreased from initially 11.5 to 7% at 200°C annealing temperature, for higher annealing temperature it is stabilized. This means that the intermixing and doping effects occur right after the deposition but do not improve the cell with annealing. On the contrary the degradation is due to the harmful diffusion of Sb or Cu atoms along the wide and Te rich grain boundaries down to the junction. This diffusion can proceed faster especially for the smaller Cu atoms.

3.2. Thickness of the applied Sb buffer layer

For the Cu/Au contact it is important to control the optimum thickness of the deposited Cu layer. Excessive Cu causes fast degradation due to diffusion and a small amount of Cu gives insufficient intermixing and doping in the bulk CdTe. The optimum Cu layer thickness is around 60 Å, which is difficult to control. For the Sb/Au contact on NP2 etched CdTe, the Sb layer thickness for an optimum efficiency is about 100 Å and the required thickness control is not stringent (Fig. 5). Yet it should be mentioned that the

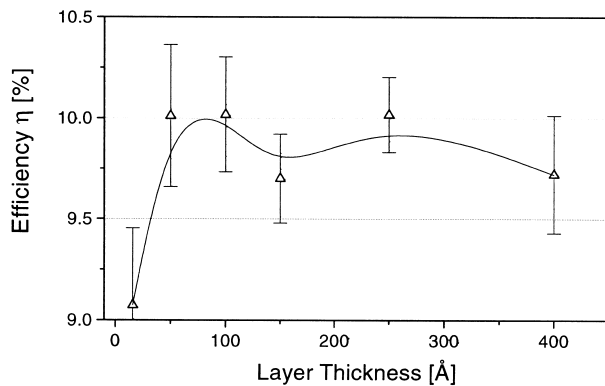


Fig. 5. Efficiency versus Sb layer thickness for the NP2 etched cells (10 s) with Sb/Au back contact. The optimum thickness is about 100 Å.

roll over of the I - V characteristics remains unaffected for different layer thickness.

3.3. Light soaking and stability

The stability of solar cells with different back contacts was measured under constant and prolonged illumination. Solar cells with the Cu/Au contact on NP2 etched CdTe degrade very fast. Within two weeks of continuous light soaking the efficiency drops down to about half of the initial value. However, the Sb/Au contacts are more stable. This can be explained on the basis of the atomic radii of the atoms. The atomic radius for Cu is 1.28 Å, for Sb it is 1.45 Å, which is about 13% larger. Therefore, the diffusion along the grain boundaries should be slower for Sb. Other publications about stability of Cu-containing back contacts report fast degradation, which is attributed to Cu diffusion as well. Efficiency degradation of 5–20% in heating cycles at 80–140°C for 25 days has been reported for ZnTe:Cu/Au back contacts [7,8]. Degradations of Cu/Mo and Cu/graphite back contact CdTe solar cells were observed but not quantified [4].

Fig. 6 shows the absolute efficiency of solar cells with Sb/Au back contacts for NP1 and NP2 optimum etched cells. The NP2 etched cell has a strong gain in efficiency in the first two days that is not compensated by the degradation during two months of light soaking. This means that despite some slow degradation, the cell is still better than the initial state. From the measurements it appears that the efficiency stabilizes after 45 days. In contradiction the NP1 etched cells have even stronger efficiency gains in the beginning but they also degrade fast and the efficiency drops far below the initial state. The degradation seems not to have stopped after the measurement period. The gain in efficiency of up to 20% in the first two days of light soaking can be explained with the filling of deep level traps in the bulk or at the junction. The degradation is caused by the diffusion of Sb and Au atoms. This diffusion is thermally assisted as well as field assisted near the junction. It would be interesting to study these effects separately. The necessary experiments are in progress. The diffusion of Sb and probably Au

atoms into the bulk and the junction suggests that Sb and Te did not react to form a stable Sb_2Te_3 compound and that the broadened grain boundaries assist in a faster diffusion of the metal atoms.

The differences in the degradation of the cells might have two reasons. The absorber layers are longer etched in NP1 than in the NP2 solution; therefore, the grain boundaries in the NP1 etched layers are likely to be wider. The diffusion of Sb is then faster in the NP1 etched cells. The structural quality of the Sb layer might also influence the quantity of Sb atoms that diffuse into the cell.

4. Conclusions

Etching with a mixture of concentrated nitric and phosphoric acid (NP etch) produces a low resistive Te-rich surface on the CdTe absorber layer. The efficiencies of the as-deposited solar cells with Sb/Au back contacts are high (up to 12.5%) despite a strong roll over in the I - V characteristics. All solar cells with Sb/Au and Cu/Au back contact on NP etched CdTe do not require annealing. However, it is not possible to get rid of the roll over in the I - V characteristic through annealing unlike that for the solar cells with Cu/Au back contacts on BrMeOH etched absorber layers. Therefore, the roll over disappears by annealing at 200°C.

Cu/Au as well as Sb/Au back contacts show typical diffusion, which is causing degradation. Nevertheless, the degradation for the Sb/Au back contacts is by far not as strong as for the Cu/Au contacts. After two months of continuously light soaking the efficiency of one set of solar cells with Sb/Au back contacts was even better than the initial efficiency. Also, in comparison to the published stability studies from other groups that use Cu-containing back contacts, the stability of the investigated Sb/Au back contacts seem to be much better. Degradation might also be a problem due to the Au diffusion but further experiments

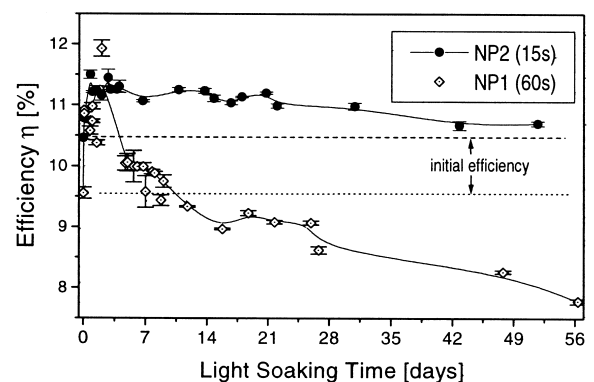


Fig. 6. Cell efficiency versus the light soaking time. The graph shows results for NP1 and NP2 etched cells. Both type of back contacts show a strong efficiency gain in the first two days before they start degrading. For the NP1 etched cells the degradation is fast and strong, whereas the NP2 etched cell degrades slowly and has still better efficiency after two months of light soaking compared to the initial state.

are necessary to identify the diffusing atoms. We believe that the diffusion of metal through the grain boundaries is not the only reason for the degradation of the solar cells. Electrical conductivity of grain boundaries and segregation are also important for the stability of the solar cells. Therefore, a strong etching of the grain boundaries is not desirable.

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