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Development of efficient and stable back contacts on CdTe/CdS solar cells

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Abstract

To make CdTe/CdS solar cells highly efficient, a Cu containing back contact (BC) is generally used. These cells degrade due to Cu diffusion to the front contact which causes shunting; this is shown with secondary ion mass spectroscopy (SIMS) depth profiling. To get a stable but still highly efficient cell, different BC materials and etching treatments were investigated. Chemical etching creates a back surface field (BSF) due to a p^+-doped Te-rich CdTe surface. To overcome the naturally existing Schottky barrier between p-CdTe and any metal, a thin buffer layer was evaporated prior to the metallization. Amongst the many investigated BC materials, the most suitable are Sb or Sb_2Te_3 as a buffer and Mo for metallization. These cells showed high stability under accelerated tests corresponding to 70 years. © 2001 Published by Elsevier Science B.V. All rights reserved.

Keywords: Back contact; Stability; CdTe; Thin films; SIMS; Solar cells

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1. Introduction

To form an ohmic contact on p-CdTe, a metal with a work function > 5.7 eV is needed. Such metals are not available, therefore, a Schottky barrier is formed at the BC. To overcome this problem a heavily p-doped CdTe surface is created by chemical etching [1,2] and a buffer layer of high carrier concentration is often applied. As a result, the barrier width is decreased and the tunneling barrier formed is quasi-Ohmic. Usually Cu is used as a buffer material or dopant for the BC. The cell yields a high FF and Voc in the beginning, but subsequently efficiency degrades due to Cu-migration.

Investigations of back contact materials like Cu/Au [2], Cu/graphite [2], Cu-doped ZnTe [3] with Au or Ni metallization, Cu/Mo [4] or just Au are reported. Romeo et al. [4] have demonstrated that rf-sputtered Sb_2Te_3 is a suitable buffer material for high efficiency cells. A degradation in efficiency up to 20% is observed when cells with ZnTe:Cu/Au BCs are annealed at 140°C for 25 days [3]. Our paper describes a study on the long term stability of CdTe solar cells developed with vacuum evaporated BC buffer layers, such as Sb, Sb_2Te_3 and Cu. It shows the influence of metallization on the PV performance.

2. Experimental details and results

2.1. Etching of CdTe and deposition of the back contact

Solar cells were developed on closed space sublimated (CSS) CdTe/CdS layers which were activated with a $CdCl_2$-treatment [8]. Prior to the deposition of the BC materials, the CdTe surface was etched with either a dilute solution of bromine in methanol (BrMeOH etch) or a mixture of nitric and phosphoric acid in water (NP etch). This etching cleans the CdTe surface from oxides and other contamination. It smoothens the surface and creates a Te-rich layer, which effectively results in a p^+-doped surface layer that produces a BSF [6]. Despite this beneficial effect, the chemical etching also widens the grain boundaries

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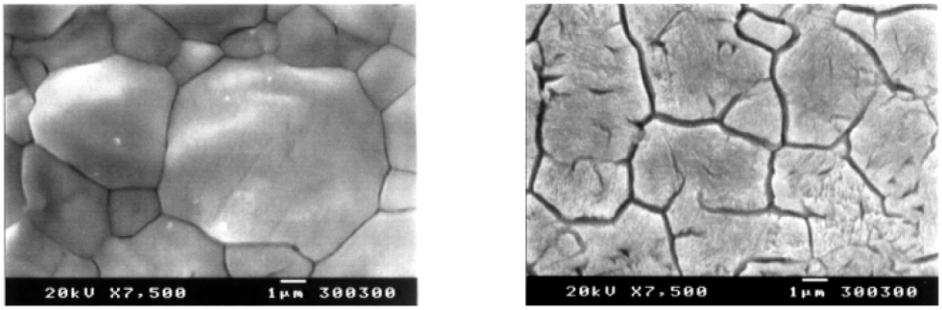

Fig. 1. SEM images of the CdTe morphology after etching. The BrMeOH etch (left) affects the morphology less than the NP etch (right) which smoothens the surface and widens GBs.

(GB) and makes the GB-surface Te-rich, see Fig. 1. This is detrimental to the cell stability, because the Te-rich GB surface may provide a conducting link between the BC and the pn-junction and the widened GB will enhance the metal diffusion into the CdTe down to the front contact. After the chemical etching, a thin (10–100 nm) buffer layer of either Sb, Sb_2Te_3, Te/Sb_2Te_3 or Cu was vacuum evaporated (PVD). The layers of Sb_2Te_3 were grown at a substrate temperature of 150°C. Sb and Cu were deposited at room temperature. The XRD patterns of the Sb_2Te_3 layers indicate that they grow stoichometrically; extra peaks corresponding to larger fractions of elemental Te or Sb are not observed. The BC was completed by metallization with a vacuum evaporated Au layer or a sputtered Al or Mo layer (500 nm).

2.2. Accelerated testing of stability

Long term stability tests were carried out in a climate chamber where the non-encapsulated cells were kept in air with 40–65% relative humidity. The cells were continuously illuminated in open circuit conditions with 1 sun (1000 W/m^2, halogen light similar to AM 1.5) at a cell temperature of 80°C. Following the estimates of Hiltner [5], we assumed a modest life time acceleration factor of 100 compared to the duration in the field. In the beginning, stability tests were made with different BC combinations at a cell temperature of 65°C (Fig. 2), which corresponds to an acceleration factor of 50. The cells are classified as stable if they decrease in efficiency by less than 10% within 40 years. All tested cells had an initial efficiency in the range from 9.5% to 10.5%. The efficiencies of cells with Au or Al metallization or a Cu buffer layer degrade severely with time. Cells with Mo metallization and buffer layers of Sb or Sb_2Te_3 do not degrade; they even show some improvement after the initial illumination in the first few days (Fig. 2). This increase in efficiency can be explained by two effects: the saturation of recombination centers in the CdTe bulk and the trap states in the interface region and the chemical reaction/interdiffusion to form an optimum compound at the interface. This is particularly the case for Sb based BCs which are grown at room temperature and are not annealed after deposition. Long term stability tests at elevated cell temperatures of 80°C indicate that Sb/Mo and Sb_2Te_3/Mo BCs yield stable cells for which the efficiency increases over a long period before slow degradation occurs. After 70 years accelerated testing time,

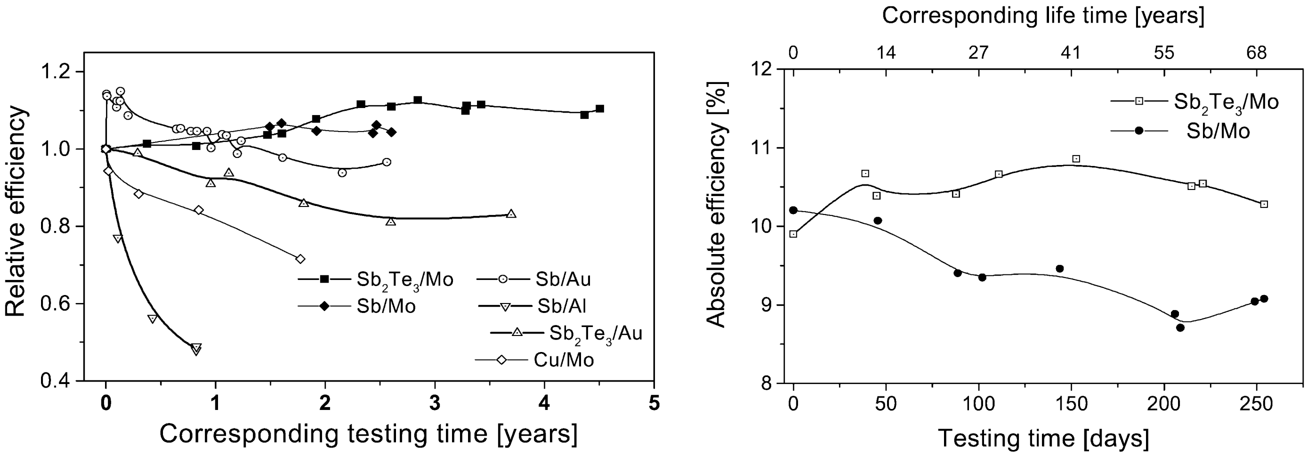

Fig. 2. Accelerated stability tests at 65°C (left) for solar cells with different back contacts; test of stable cells with Mo metallization at 80°C (right).

the efficiency is still above the initial value. The gradual increase in efficiency can be explained as described above. The slight degradation is probably due to the oxidation of the BCs in the humid ambient at 80°C, because the cells were non-encapsulated. Oxidation affects the contact barrier and, therefore, the effective resistance of the cell. The efficiencies degraded mainly due to the drop in FF and Voc, accompanied by an increase in contact barrier height. The cell with Sb/Mo BC degrades moderately from the beginning, approximately 8% relative efficiency in the first 150 days, corresponding to an accelerated stability testing of 40 years. In the end, these cells degraded by 12% in relative efficiency on a time scale of 70 years with a tendency towards saturation.

2.3. Carrier concentration and contact barrier height

CV-measurements at 100 kHz with an excitation amplitude in the range of 5–20 mV were performed to calculate the carrier concentrations (CC) and barrier heights (BH). The doping profiles of all cells are characteristically similar (Fig. 3). The effective CC in the vicinity of the pn-junction is in the range of 10^{13}–10^{14} cm^{-3}. The CC rises towards the BC where it is one order of magnitude higher, suggesting that CdTe is doped due to the BC materials and etching. BHs above 250 mV limit the current at high forward bias [7]. The CC at the BC of cells with Sb_2Te_3/Mo is the highest, which corresponds to a low BH of 0.34 eV [7]. Although the CC near the BC of the Cu/Mo cells is lower than that of the Sb_2Te_3/Mo cells, a BH of 0.22 eV is low enough to create a quasi-ohmic contact. Cells with Sb/Mo BC have the lowest CC and the highest BH with 0.6 eV. BH values have been derived from the linear parts of the $1/C^2$-plots.

2.4. Secondary ion mass spectroscopy depth profiling

SIMS depth profiling was made on cells with Sb/Au, Cu/Au, Sb/Mo and Sb_2Te_3/Mo BCs using a CAMECA-IMS3F system and a Cs^+-ion beam of 200–550 nA. Profiles of Au and Cu in Fig. 4 clearly show the indiffusion from the surface of CdTe into the bulk and then towards the junction. An accumulation of Cu and Au at the front contact interface is observed. The metals (Cu and Au) diffuse under thermal and electric fields and contribute to the shunting of the solar cells in conjunction with the Te-rich surface of the GB [1,7]. Within the detection limit, there was no indication for Mo or Sb_2Te_3 to diffuse from the BC into the bulk of CdTe [8]. An intermixed region of $CdTe_xS_y$-phase (> 1 μm) creates a smooth pn-junction.

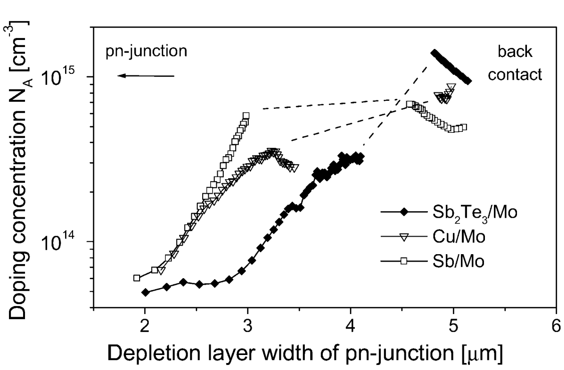

Fig. 3. Doping profiles of cells with different buffer layer and Mo metallization.

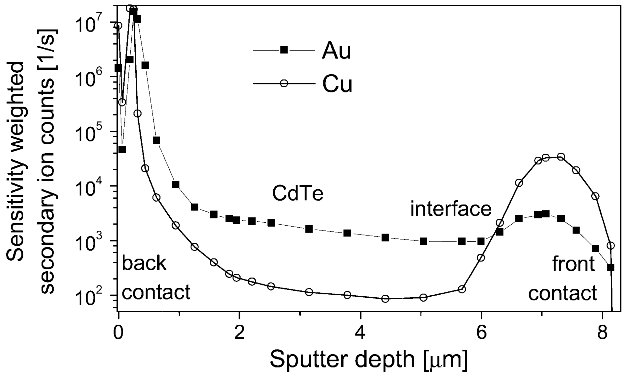

Fig. 4. SIMS depth profiling of a CdTe/CdS cell with Cu/Au back contact.

3. Conclusions

Solar cells with vacuum evaporated BCs were developed. Etching solutions influence the CdTe morphology and grain boundaries, and produce Te-rich (conducting) surfaces. Sb and Sb_2Te_3 BC buffer layers with Mo metallization on CdTe yield long term stable CdTe/CdS solar cells. A minor degradation in efficiency, particularly for Sb/Mo BCs, could be due to oxidation of the non-encapsulated BCs. Further CV-characterization and SIMS -measurements will help to identify the degradation mechanisms, especially the role of etching and metal migration.

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