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Investigations of a buffer layer grown on a CdTe surface

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Abstract. The possibilities for substitution of several contact pre-deposition procedures by one technological step have been investigated with the aim of improving solar cell performance and reduction of the corresponding production cost. Growth of a low-resistance buffer layer on the surface of a CdTe based solar cell is interesting not only from a practical point of view but also concerning the structural and compositional changes introduced in the CdS–CdTe heterostructures. Information about the electrical properties of the layers involved is presented and discussed with respect to the further extension of this method.

1. Introduction

Despite the fairly large volume of work done to study different contacts to p-CdTe, a range of problems related to the development of stable low-resistance electrodes still remains. The new trend is to plan each technological operation prior to establishing solar cell production. For example, the contact pre-deposition procedures have to be compatible with the main layer preparation processes. If these are vacuum evaporation or close space sublimation (CSS), the traditional treatment with CdCl₂ is not suitable, when sample cooling from a temperature typically of between 500 and 300 °C down to room temperature followed by dipping in a solution of CdCl₂ is required. This is followed by thermal treatment at 400 °C for 30 min and cooling down to room temperature again. For a low-cost cell production it is attractive to replace all these operations by one technological step, but such a simplification can be realized through a detailed study of the reactions which occur on the CdTe surface during cell processing. The results of an investigation in this direction are presented in this paper. Some experimental data about the properties of ZnTe layers grown on the CdTe surface have been discussed revealing the advantages of such buffer layers for back contact improvement.

2. Experiments

The solar cells considered were obtained according to the following procedures: on conductive glass with 400 nm SnO₂ coating, a CdS layer was deposited electrochemically or by close space sublimation. The former had a thickness up to 50 nm and the latter 200–500 nm. On CdS a 5000 nm thick CdTe layer was deposited by CSS in N₂ with 3.5% of O₂. Instead of the screen-printed carbon paste electrodes, Ni or CVD-W and Mo [1] were used as back contact. Au or Cu–Au electrodes were evaporated on several samples for comparison. In our former experiments the cells were subjected to the standard CdCl₂ thermal treatment in Ar at 400 °C

for 30 min [2]. Recently this was replaced by annealing of the layers in contact with a carbon block containing Cd or Cu salts, as described in [3]. Then the etching was done in $\text{HNO}_3\text{--H}_3\text{PO}_4\text{--H}_2\text{O}$ mixtures with different component ratio. After this procedure a ZnTe buffer layer was deposited electrochemically. A water solution of 0.1 M ZnCl_2 , 2×10^{-4} M TeO_2 and 2×10^{-4} to 6×10^{-4} M CuSO_4 was used at $\text{pH} = 3.5$. If the temperature is 55°C a 20 nm ZnTe layer can be deposited for 15 min. In some cases the buffer layer deposition was realized immediately after the thermal treatment in contact with a block of modified carbon material (avoiding chemical etching).

For several samples x-ray diffraction (XRD) analysis was performed with a DRON-2 diffractometer and electron dispersive spectroscopy (EDS) by a JEOL 35CF system.

Table 1 presents EDS data for selected CdS–CdTe heterostructures. The values for oxygen are from x-ray photoelectron spectroscopy analysis [3] but those for chlorine were found to be less than 1% and so are not included in the calculation. Sample 1 was not subjected to any treatment (as grown). Sample 2 was annealed in Ar at 400°C for 30 min after a dipping in the standard CdCl_2 solution. Sample 3 was thermally treated at the same temperature for the same time and then etched in $\text{HNO}_3\text{--H}_3\text{PO}_4\text{--H}_2\text{O}$ solution (10:70:20) for 60 s. Sample 4 was annealed at 150°C for 2 h and etched in the same solution as sample 3. During the thermal treatment of sample 5 the CdTe layer was in contact with a 3 mm thick carbon block cut from a deposit formed on the electrodes during AC arc discharge in a vacuum chamber [2]. CdCl_2 was introduced into the block by alcohol solution.

Table 1. Relative elemental amounts determined by EDS (at.%).

| Sample No | Te | Cd | O | Cd/Te ratio |
|-----------|------|------|------|-------------|
| 1 | 43.6 | 42.2 | 14.2 | 0.97 |
| 2 | 35.6 | 53.4 | 11.0 | 1.5 |
| 3 | 64.5 | 20.4 | 15.0 | 0.32 |
| 4 | 64.3 | 20.5 | 14.9 | 0.32 |
| 5 | 48.0 | 37.3 | 14.7 | 0.76 |

After etching and after ZnTe deposition, measurements of the sheet resistance were made. The values obtained changed by less than 20% along the whole area of the cells. At the end on the same heterostructures back contacts have been evaporated. The presence of a ZnTe intermediate layer makes the contact characteristics almost independent of the metal used (Au, W, Mo). The photovoltaic parameters presented below have been measured with Au contacts at irradiance of 100 mW cm^{-2} .

Table 2 is an illustration of the cell performance changes obtained by modification of certain technological operations. Samples 1, 2 and 3 were subjected to the same treatments as the corresponding samples from table 1. Number 4 differs from number 3 only by the inclusion of ZnTe between CdTe and Au. Sample 5 was annealed in contact with a block of modified carbon (alternative CdCl_2 treatment) and etched before the deposition of ZnTe. Sample 6 was obtained by the same procedures but etching was omitted.

The higher conductivity of the buffer layer, a measure of which is the sheet resistance, was found to be sufficient for lowering the contact resistance R_c . On some samples values of R_c below $1 \Omega \text{ cm}^{-2}$ were obtained but this was connected with a decrease of V_{oc} .

It is evident from table 2 that the alternative annealing (sample 5) secures high values of V_{oc} and FF. In addition the data for sample 6 show that the etching can be removed.

Table 2. Sheet resistance (R), open circuit voltage (V_{oc}), short circuit current (J_{sc}), fill factor (FF) and efficiency (η) after different post-deposition treatments.

| Sample No | R (k Ω / \square) | V_{oc} (mV) | J_{sc} (mA cm $^{-2}$) | FF (%) | η (%) |
|-----------|-------------------------------|---------------|---------------------------|--------|------------|
| 1 | 760 | 250 | 5.3 | 0.39 | 0.5 |
| 2 | 510 | 620 | 14.2 | 42 | 3.7 |
| 3 | 14 | 733 | 20 | 54 | 7.9 |
| 4 | 7 | 611 | 21 | 63 | 8.1 |
| 5 | 10 | 790 | 22.5 | 64 | 11.4 |
| 6 | 9 | 790 | 22.7 | 66 | 12 |

3. Discussion

Beginning with the first work [4] there were several attempts to deposit ZnTe under the contacts to p-CdTe. All of them resulted in improvement of the contact characteristics but also in reduction of V_{oc} due to shunt paths through the junction, usually along the grain boundaries, where, in the process of standard CdCl₂ treatment, molten phases of CdCl₂-Te eutectics are attracted by capillary effects [5]. As a result a substantial increase of the Cl concentration is possible. The same phenomena cause segregation of different defects at the grain boundaries and form regions of enhanced diffusion. Thus the penetration of Cu from the buffer layer to the junction during the additional annealing also increases the leakage currents determining the V_{oc} drop observed. Another reason for the unsatisfactory contact characteristics may be the excess of Cd near the CdTe surface. It is evident from table 1 that the traditional CdCl₂ thermal treatment is linked to the excess Cd on the surface. The concentration ratio Cd/Te for sample 2 is 1.5, in distinction with sample 1 (as deposited), where it is nearly 1. The subsequent etching results in extraction of elemental Te mixed with TeO₂ [3]. This explains the very low Cd/Te ratio for samples 3 and 4. The corresponding surface reactions lead to lowering of the sheet resistance but often they provoke degradation processes [6]. One of the possibilities for avoiding the aging is the application of modified carbon materials in layer thermal treatment.

In samples like No 5 a moderate deviation from stoichiometry is achieved and the improvement of the back contact properties is already not connected with lowering of V_{oc} . In addition, the introduction of O₂ in the transport gas for CSS layer deposition results in removal of microvoids, pinholes, precipitates and other defects from CdTe [7]. As it is explained in [3] the high concentration of oxygen in the samples together with the lack of TeO₂ promotes the formation of acceptor centres. In this way the combination: O₂ addition, alternative CdCl₂ treatment and ZnTe buffer layer improves the performance of the solar cells as becomes clear from table 2.

4. Conclusion

The investigations made have shown that by modification of certain fabrication steps a better correlation between them can be achieved. First the structure, in particular the grain boundary properties have been changed by O₂ addition to the N₂ flow through the deposition chamber. Then, an alternative CdCl₂ treatment has been tested and as a result the influence of the junction shunt paths on the V_{os} values has been minimized. It was found also that after such a treatment the deposition of a ZnTe buffer layer between CdTe and the back contact allows for the removal of the chemical etching procedure. The gathered information can be used in the further experiments for reduction of the CdTe layer thickness to 1 μ m. Only in these

conditions can we expect a positive effect from the back surface field obtained by inclusion of larger-band-gap layers, such as ZnTe.

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