Efficiency improvement in thin-film solar cell devices with oxygen-containing absorber layer

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The CdTe/CdS solar cell devices were grown using a dry process consisting of sputtering for the transparent conductive oxide and CdS window layers, and close-space sublimation for CdTe absorber layer. These devices were back contacted using Mo/Sb2Te3 sputtered layers following the CdCl2 activation process carried out in air. It was shown that when oxygen is intentionally introduced in the CdTe layer during its growth, this leads to a significant improvement in all the device parameters yielding an efficiency of 14% compared to 11.5% for devices fabricated in the same conditions but without intentional oxygen incorporation in CdTe. The data obtained were not altered following a light soaking. The devices were investigated by quantitative secondary ion mass spectrometry, which allowed insight into the distribution and amount of oxygen and chlorine within the entire device structure. Both impurities showed an increased concentration throughout the CdTe absorber layer. © 2005 American Institute of Physics. [DOI: 10.1063/1.2152108]

A sustained research effort has been made in the past decades towards improving the performance of CdS/CdTe solar cell devices. However, the best efficiencies achieved so far are still about 50% of the theoretically possible performance. Among the approaches used to reach this goal, only a few dealt with the doping of either the CdTe absorber layer or the CdS window layer during their growth.1,2 Unfortunately, these attempts led to conflicting results concerning the effect that such a doping could have on the behavior of the resulting device. Indeed, Boyle et al. studied CdTe/CdS solar cell devices and concluded that there was neither an obvious correlation between the reagent concentrations in the CdS bath and the solar cell efficiency of CdTe/CdS devices, nor a straightforward relationship between the impurities profiled in the device and the characteristics of the latter.2 Similarly, Altosar et al. recently reported on CdS films prepared by chemical bath deposition from solutions containing different donor impurities and found that the performance of solar cells made with the resulting different CdS layers was not noticeably affected.3 This was attributed to the fact that, for these cells, the CdS layer is not necessarily part of the heterojunction with the absorber layer, and that a working buried homojunction exists instead, where the n-type region is formed on the surface of the p-type absorber.3 However, it was recently shown that the presence of impurities in doped CdS-based thin films leads to an enhancement of the photosensitivity while the photovoltaic efficiency of these films in a metal-semiconductor junction is decreased.1

In recent works, we reported secondary ion mass spectrometry (SIMS) studies of CdTe/CdS/TCO solar cell structures depth profiled throughout using quantitative SIMS from the back4 and the front side.5 These investigations demonstrated the existence and importance of impurities in the solar cell structures and elucidated the main sources of impurities. We have also shown that the subsequent overgrowth of the CdTe absorber layer on top of the CdS window layer substantially affects both the concentration and the profile of the impurity species present in the as-grown CdS (Ref. 6).

In recent reports by different groups, the role of oxygen in CdTe solar cells was mainly investigated for devices post-growth processed in oxygen-containing environments.⁷–⁹ This investigation aimed at studying the effect, on the characteristics and performance of CdTe/CdS solar cell devices, of an in situ doping of the CdTe absorber layer with oxygen. It was found that the introduction of oxygen into the CdTe layer during its growth improves the efficiency of these devices as compared to the devices without the addition of oxygen.

The devices were grown on sapphire substrates in an attempt to avoid the impurity species such as Na, and probably also Si and O, that were shown to be more likely originating from the commonly used glass substrate.⁴,⁵ These impurities are known to have a doping effect in both CdTe and CdS materials. The sapphire substrates were 2.5×2.5 cm² and 0.5 mm thick, and were thoroughly cleaned prior to the structure deposition. The transparent conducting oxide layer was deposited by reactive sputtering at a substrate temperature around 450 °C and consisted of a fluorine-doped indium tin oxide (ITO:F) film (~1.2 μm thick) followed by a tin oxide (SnO2) film of about 300 nm thickness. Ar+O2 atmosphere was used for both layers and CHF3 was added in the case of ITO:F. The CdS:F layer (~80 nm) was also deposited by reactive sputtering using Ar and CHF3 flows at a substrate temperature of 200 °C and a total pressure of 5×10⁻² mbar. Close-space sublimation (CSS) was used for the growth of the 6–8 μm thick CdTe layer. During the CdTe growth of one of the devices, oxygen was intentionally incorporated in situ by letting O2 gas into the CSS chamber. For the purpose of comparison, the CdTe layer of the other device was grown under the same conditions but without oxygen introduction. Both device structures then underwent a CdCl2 processing via thermal evaporation of CdCl2 on top of the structures and air annealing (400 °C for 30 min), fol-
Table I recapitulates the parameters of 1 cm² solar cell from both devices grown, respectively, with and without oxygen introduction into CdTe. The solar cell area is 1 cm² in both cases.

<table>
<thead>
<tr>
<th>Condition</th>
<th>V_{oc} (mV)</th>
<th>J_{sc} (mA/cm²)</th>
<th>Fill factor</th>
<th>Efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without oxygen in CdTe</td>
<td>780</td>
<td>23</td>
<td>0.64</td>
<td>11.5</td>
</tr>
<tr>
<td>With oxygen in CdTe</td>
<td>812</td>
<td>25</td>
<td>0.69</td>
<td>14</td>
</tr>
</tbody>
</table>

The concentration of oxygen in the CdTe layer is about 1 order of magnitude higher (from ~10^{19} to ~10^{20} cm^{-3}) especially from the middle of the layer through to the CdTe/CdS interface, when it is intentionally in situ introduced compared to the device without oxygen incorporation. The near surface region of the CdTe layer exhibits a concentration of O around 5 × 10^{19} cm^{-3}. Chlorine, however, is found to have a concentration in CdTe on average 2–5 times higher when oxygen is introduced into the CdTe layer during its growth. As for the distribution of these two elements within the CdTe layer, O and Cl show rather flat profiles for the sample without O incorporation while, for the sample with O incorporation, they exhibit nonuniform distributions particularly for Cl. This indicates that the in situ doping of the CdTe layer with O is not only efficient but also favors the incorporation of Cl into the CdTe layer following the CdCl_{2} activation process. We believe that oxygen incorporation in CdTe and the enhanced concentration of Cl in CdTe related to the presence of oxygen may both contribute to the improvement of the solar device parameters. In other words, at least in part, O and consequently Cl are not neutral in CdTe but seem to be electrically active and/or form electrically active complexes within the CdTe absorber layer, leading ultimately to an enhanced overall performance of the CdTe/CdS solar cell. This seems to be the case despite the well-known compensation effect in CdTe. Although O is isoelectronic, its role in CdTe has been a subject of considerable discussion.^{7–10} Cl can be incorporated as either a donor, single substitutional impurity, or as an acceptor, the Cl A-center. The mechanism through which the device improvement occurs deserves further investigation.

In summary, we have shown that an intentional in situ introduction of O in the CdTe absorber layer of the CdTe/CdS solar cell device leads not only to an order of magnitude increase in the amount of O but also to an enhanced Cl concentration in CdTe as a consequence of O presence. This increase in the concentration of both O and Cl in CdTe was shown to affect directly the resulting device by improving all its parameters, and leading to an efficiency of 14% compared to 11.5% when O is not intentionally incorporated in CdTe during its growth.

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