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Study of spatially resolved impurity diffusion in CdTe solar cells using voltage dependent quantum efficiency

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Abstract

The performance stability of CdTe/CdS solar cells is strongly determined by diffusion of impurities from the back contact into the absorber layer and hetero-junction. Impurity migration changes the effective carrier concentration and barriers in the device by compensation of donors or acceptors and by creation of defect centres. The CdS window layer is particularly affected by this phenomenon, since the impurities tend to accumulate there. This can be characterised by measuring the voltage dependent, the so called apparent quantum efficiency (AQE) in the blue wavelength region, while the back contact can be analysed by the AQE in the IR. CdTe/CdS cells with different back contact materials have been stressed in different conditions and ambiences. When thermally stressed in presence of oxygen, enhanced AQEs were observed for cells containing Cu, while cells containing Sb showed negligible changes, in the UV range as well as in the IR range. In comparison, vacuum-stressed Cu containing cells showed lower AQEs, but still higher than non-stressed cells. Results of the stressing tests for different materials and in different conditions have been analysed and interpreted using the recently developed model of a modulated barrier in the CdS bulk.

Keywords: Apparent quantum efficiency; Impurity diffusion; CdTe; Thin films; Solar cells

1. Introduction

The long term stability of CdTe solar cells is an important and widely studied issue that is determined by the distribution and diffusion of impurities in these devices. Unlike in group IV or III–V semiconductors, impurities are less effective for doping due to the ionic character of II–VI compounds like CdTe or CdS. Therefore, the impurity dopants often segregate or are compensated. On the other hand, small concentrations of impurities below detection limits of most techniques degrade the long term performance of solar cells. To be able to detect and identify impurities in the cells, direct methods with a good resolution like secondary ion mass spectroscopy (SIMS) are needed. However, SIMS depth profiling is destructive and limited in its spatial resolution because initial surface roughness and additional sputtering blur the depth information.

This study correlates photoelectronic changes to impurity diffusion using voltage dependent quantum efficiency measurement, which were interpreted on the basis of the recently developed CdS bulk barrier model [1,2]. The apparent quantum efficiency (AQE) can be much higher than unity in the 'blue' and 'IR' spectral range [3]. The behaviour of the AQE is explained by the above mentioned model with a modulated barrier photodiode (MBP) in the front region of the cell [1] and a back contact barrier. The existence of the MBP is a consequence of the activation with Cl, the intermixing of CdTe with CdS and impurities in the CdS [1,4]. The CdS near the metallurgical interface becomes intrinsic due to the compensation of donors by acceptors, while the intermixed CdS_xTe_{1-x} is n-type. Consequently, a hump in the conduction band forms in the depleted CdS and is modulated by light. The calculated band diagram focusing on the front part of the cells is sketched in Fig. 1 in illuminated and dark condition. The AQE at forward bias can show two distinct features: a peak in the blue response, which the model explains as a consequence of the MBP; and a peak in the IR response at the band

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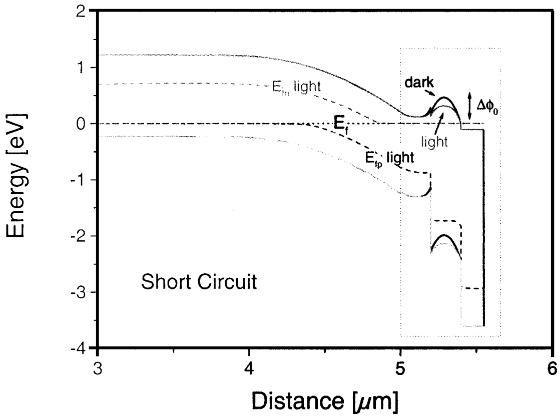

Fig. 1. Calculated band diagram of CdTe solar cells with a MBP. The barrier modulation is shown for dark and the illumination conditions.

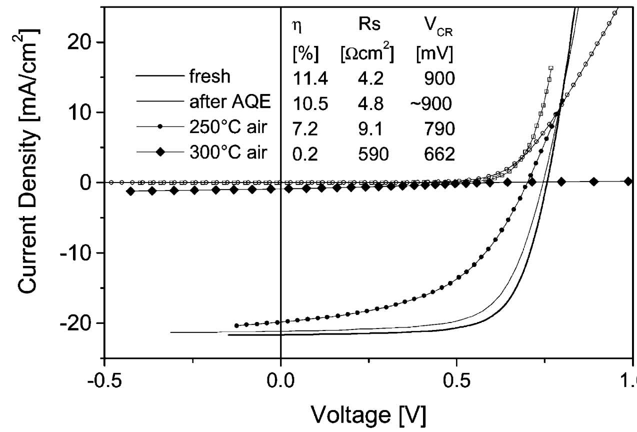

Fig. 2. *I–V* characteristics of cells with Cu/Au back contact stressed in air. Performance decreased with increasing stressing temperature.

edge of CdTe, which almost certainly results from a second barrier with photo transistor like action from the back contact [5]. Latest measurements evidence the photo transistor action behaviour [6], however, the IR response peak is subject of current investigation [7,5] and the location of the latter is debated. The response peaks are caused by secondary currents with negative direction (in respect to the photo current), as can be taken from the phases of the AQEs. This non-destructive and easy to apply method provides additional spatial information. Cells with different back contacts were stressed to enhance the impurity diffusion and the AQE technique was applied to monitor the photoelectronic changes caused by the diffusing impurities.

2. Experimental details and results

The CdTe cells used for this study have a 0.2 μm thick CdS layer and approximately 6 μm thick CdTe layer both deposited by close spaced sublimation [8]. The cells were activated in $CdCl_2$ vapour without oxygen prior to standard etching [9] and back contacting with either Cu/Au (6 nm/50 nm) or Sb/Mo (10 nm/200 nm), which yielded devices of initial efficiencies in the range of 10–11%. These cells were stressed either in vacuum or air at 250 °C for 45 min. Standard lock-in-technique was used to measure the AQE in the range of 300–1050 nm using a grid-monochromator without additional bias illumination. A custom made trans-impedance-amplifier was used to apply bias voltage in order to keep the cell at the adjusted work point, while signal and phase were monitored. Cell degradation was analysed by current–voltage (*I–V*) characterisation.

3. Performance degradation by thermal stressing

The thermal stressing is expected to accelerate impurity diffusion and enhance defect mobility, whereas compositional changes should be excludable due to the previous $CdCl_2$ treatment. The relevant parameters from the *I–V* characteristics (Figs. 2 and 6) of the cells before and after stressing are listed in Table 1. The general trend of degradation is associated to an increase in series resistance and a decrease of the voltage V_{CR} where the cross-over between light and dark *I–V* characteristics occurs. A certain degree of degradation was already observed directly after AQE characterisation, which included biasing >1 V up to 1 h. The observed degradation is most likely a consequence of the metastable nature of CdTe/CdS cells, explained also by the MBP model, possibly recovering with time. Fig. 3 shows a slightly stronger stressing degradation of Cu/Au contacted cells in vacuum (compared to air-stressing), which might be explained by a temperature discrepancy in different furnaces. The quantum efficiencies (at 0 V) before and after stressing are shown in Fig. 4. The degradation is probably determined by an effective diffusion length decrease in CdTe, which can be deduced from the lower response in the 1R and is most likely

Table 1
Cell parameters from *I–V* characteristics of stressed (non-stressed) cells

BC/stressing	J_{SC} (mA/cm²)	V_{OC} (mV)	FF (%)	η (%)	R_S (Ω cm²)	R_p (Ω cm²)	V_{CR} (mV)
Cu/Au vacuum	18.3 (21.9)	662 (746)	46 (67)	5.6 (10.9)	8.7 (4.6)	153 (1300)	705 (900)
Cu/Au air	20.3 (21.3)	700 (749)	50 (67)	7.1 (10.7)	9.1 (4.2)	215 (1300)	790 (900)
Sb/Mo air	19.9 (21.2)	706 (769)	48 (63)	6.8 (10.2)	–	1200 (4000)	– (807)

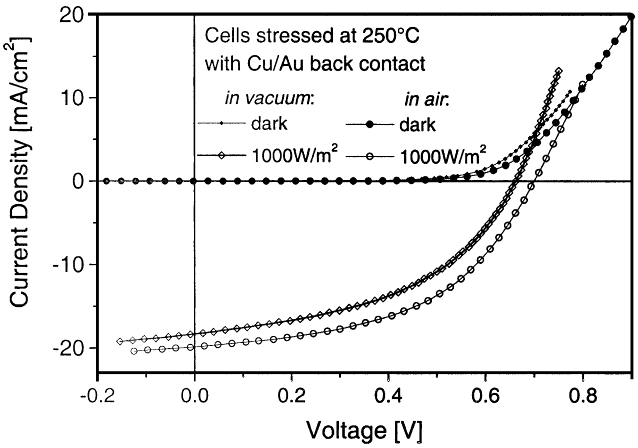

Fig. 3. Comparison of I–V characteristics of cells stressed at 250 °C in air and in vacuum. The vacuum-stressed cells degraded slightly more.

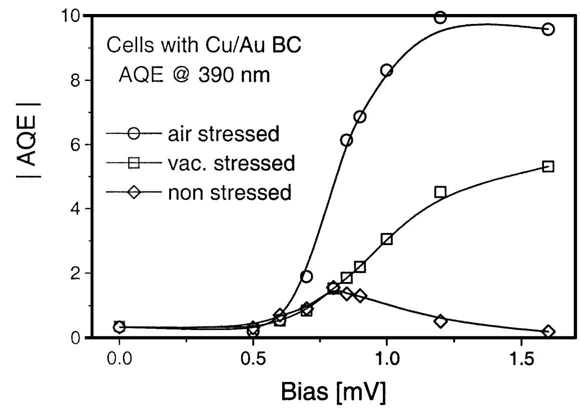

Fig. 5. AQEs vs. bias at 390 nm of cells with Cu/Au back contacts. The stressed cells exhibited an increased AQE at high forward bias, which was approximately two times higher for the air-stressed cells compared to the vacuum-stressed cells.

caused by recombination centres formed by impurity diffusion. To get more information on the degradation at other work points, AQE_λ characterisation was performed at a single wavelength. Fig. 5 shows AQEs at 390 nm, where the blue gain response is highest, as a function of bias voltage for Cu/Au contacted cells. Up to 0.8 V vacuum-stressed cells as well as non-stressed cells exhibit the same AQEs. For higher bias the AQEs of the vacuum-stressed cell increased gradually showing a tendency to saturation above unity, while for the non-stressed cell it dropped back below unity. According to the MBP model, the larger gain in AQE is explained by a barrier increase, which is two times higher for the air-stressed cells. The increase of the barrier is caused by further donor compensation, which together with the role of oxygen will be discussed in the following section. The maximum in the $AQE_\lambda(V)$ occurs when the back contact limits the current at high forward bias and a further lowering of the modulated barrier (MB) has no effect on the AQE gain any more.

Cells with Sb/Mo contacts show a different degradation pattern. The performance degradation of air-stressed cells is comparable to the one of Cu/Au contacted cells, see Fig. 6 and Table 1, yet there remains a higher parallel resistance (obtained by fitting the I–V with a 1-diode-model) indicating fewer recombination losses in cells with Sb/Mo back contacts. The effect of oxygen is an increased back contact barrier, evident in a strong roll-over of the I–V characteristics conditioning a very low FF. The AQEs of the cells with Sb/Mo contact at 390 nm differ from the Cu/Au contacted cells (Fig. 7), since the complete AQEs stay below unity and only the non-stressed cells exhibit a small gain ($\approx$0.7 V), while the air-stressed cells exhibit none. The AQEs of air-stressed cells at forward bias are slightly higher than of non-stressed cells but lacking the

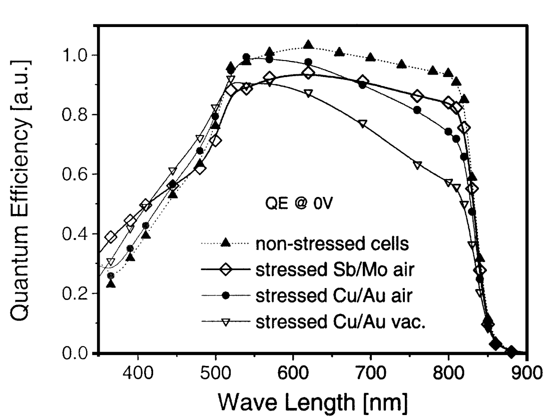

Fig. 4. External relative quantum efficiencies of stressed and non-stressed cells. All stressed cells exhibited a decreased quantum efficiency with especially decreased infrared response of Cu/Au contacted cells indicating reduced diffusion length.

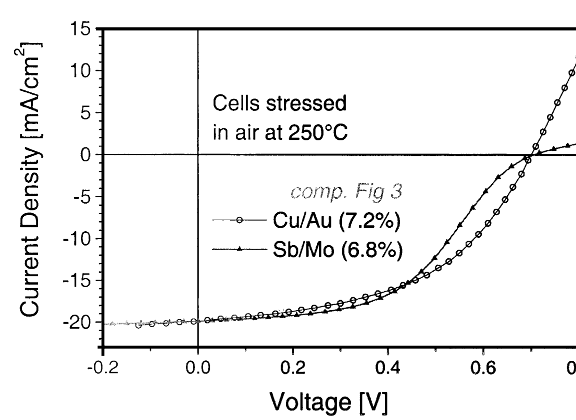

Fig. 6. I–V characteristic comparison of thermally stressed cells with Cu/Au and Sb/Mo back contacts. The Sb/Mo contacted cells exhibited a strong roll-over whereas the Cu/Au contacted cells exhibited a strongly decreased parallel resistance.

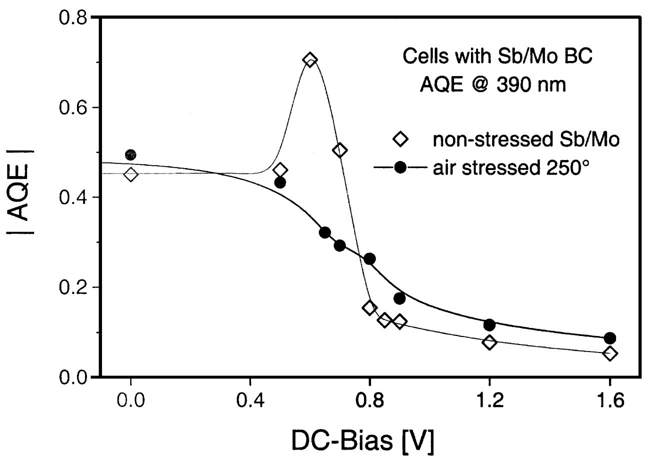

Fig. 7. AQEs vs. bias at 390 nm of cells with Sb/Mo back contacts. The air-stressed cells exhibited no increase of AQE in contrast to Cu/Au contacted cells.

gain. According to the model, the MB must have been lowered to the point where no gain was observed.

The AQEs provide further information in the IR region near the band edge of CdTe, where the AQEs, are determined by the barrier of the back contact diode, that can reach into the absorber preferentially via the grain boundaries. Fig. 8 shows AQEs at 1.2 V bias in the IR region between 740 and 880 nm for all cells. Air-stressed cells exhibit a pronounced gain at the band edge of CdTe in contrast to non- and vacuum-stressed cells which show no gain. For cells with Cu/Au contact the IR–AQE gain is 4–5 times higher than for cells with Sb/Mo contact. To achieve this gain, the consistent model explanation requires an increase of the back contact barrier caused by oxygen.

4. Discussion

The degradation of the stressed cells can be understood by means of the AQE characterisation explained by the MBP model and direct measurements of impurity accumulation in CdS by SIMS depth profiling [6,10]. Additional degradation may occur due to diffusion of impurities originating from the source materials, which commonly reduce the long term stability of the CdTe/CdS solar cells. Since identical cell layers have been used for this study, any additional impurity diffusion would have had a similar effect on all the measurements, which is therefore neglected. Since Cl, Cu, Au or O act as acceptors in CdS [11], they enhance the donor compensation that is required for the existence of the MBP and hence, increase the height of the hump in the conduction band in CdS. These acceptors are typically located at mid gap in CdS [11,12], so they can act as effective recombination centres. The diffusion of Cu (and Au), preferably via grain boundaries into CdS fulfils the requirements of the model to generate the observed AQE gains. In this situation, the diffusion of Cu (and Au) is promoted in the presence of oxygen, facilitating the IR–AQE gain by increasing the barrier at the back.

Applying the MBP model to the AQEs of the Sb/Mo contacted cells leads to the conclusion that the stressing results in a lowered MB, which also explains the slight increase in the blue response. Due to the larger atomic radius of Sb compared to Cu, the diffusion of Sb should be significantly slower, as already observed in performance stability tests [9]. In accordance to the MBP model it can be concluded that Sb does not diffuse into CdS. Even if a small amount of Sb is diffused into CdS, there should be no donor compensation effect and Sb should act electronically neutral, i.e. not detrimental to the photovoltaic properties. SIMS measurements have shown an accumulation of very small quantities of Sb at the CdS/TCO interlace. Taking the difficulty of SIMS signal quantification due to matrix effects into account, SIMS profiles should be carefully interpreted regarding the above discussed observations.

The IR–AQEs reveal the effect of oxygen on air-stressed contacts indicating an increased barrier. Considering the complete AQEs, the Cu/Au contacted cells indicate a diffusion and accumulation of Cu and maybe even Au into the CdS layer under stressing, while for cells with Sb/Mo contacts, the back contact material diffusion can be neglected. Since the air-stressed Sb/Mo contacted cells exhibit no UV–AQE gain, an effect of oxygen on the MBP can also be neglected. These results confirm the oxygen promoted Cu diffusion, as previously suggested [10]. The diffused Cu has no additional doping effect in the absorber, indicated by

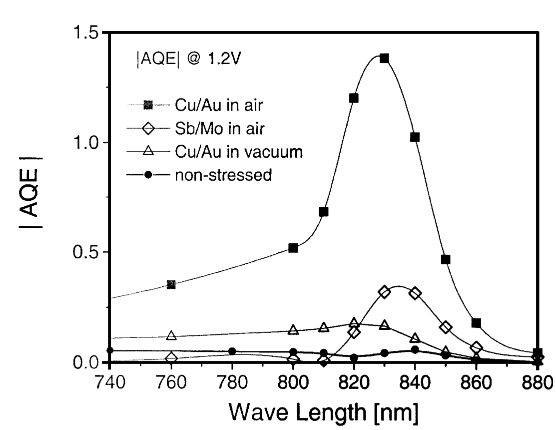

Fig. 8. AQEs vs. wavelength at 1.2 V of stressed and non-stressed cells. Air-stressed cells exhibited a pronounce increase of AQE approximately 830 nm.

the $I-V$ characteristics. SIMS reveals a Cu concentration in CdTe lower by orders of magnitude in comparison to CdS. The IR–AQE of the air-stressed cells indicates a further diffusion of the Cu/Au back contact into the CdTe (presumably via grain boundaries) absorber after stressing. This is based on the high AQEs of Cu/Au contacted cells above 800 nm where wavelengths with lower penetration depths are collected as negative current. In contrast, in Sb/Mo contacted cells the AQEs between 800 and 810 nm crosses 0 together with a phase shift close to π, only producing negative current above 810 nm. This fact supports the conclusions that Sb and Mo do not diffuse into CdTe.

5. Conclusions

Cells with Cu/Au and Sb/Mo back contact have been thermally stressed in air and in vacuum. Assisted by AQE measurements, the MBP model led to conclude that thermal stressing enhances the diffusion of Cu (and Au) from the back contact of the cell into the CdS layer where is accumulates. Besides, Cu diffusion it further promoted by the presence of oxygen. However, there is no indication of diffusion of Sb or Mo from the Sb/Mo back contact. In case of Cu contacts, air-stressing increases the back contact barrier as effect of oxygen and diffusion. The AQE approach to study the effects of impurity diffusion is a non-destructive analyses allowing the correlation between photoelectrical and compositional changes in the solar cell. The performance of CdTe/CdS solar cells is limited by the MBP. The characterisation of the barrier in the front is an important step to identify the efficiency losses, which may help to improve the efficiency and stability of CdTe/CdS solar cells.

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