JOURNAL OF MATERIALS SCIENCE: MATERIALS IN ELECTRONICS **11** (2000) 525–530

Effect of interdiffusion and impurities on thin film CdTe/CdS photovoltaic junctions

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We have used low temperature photoluminescence (PL) to study thin film CdTe/CdS solar cell structures. The devices were produced by close space sublimation (CSS) and have undergone a post-growth treatment, a vital step in increasing device efficiency. The treatment consisted of evaporating a thin layer of $CdCl_2$ onto the back CdTe surface and heat treating in air at 400 °C for between 10 and 120 min. This produced a range of device efficiencies from 2% to 9%. The efficiency improvements are the result of a complex interaction between the $CdCl_2$, impurities and sulfur interdiffusion. The structures were prepared for PL by a chemical bevel etching technique which allows the luminescence emission to be studied as a function of depth throughout the sample. The main features in the PL spectra have been identified as being due to the Cl-*A* center and the Te-dislocation-related *Y* luminescence band. Using PL we have quantified the S diffusion into the CdTe which has a maximum of 20% at the interface in the most efficient samples. We have also obtained the profiles of recombination and non-radiative recombination centers in the device. We observe correlations between impurity centers and device efficiency which can help explain the effects of the $CdCl_2$ treatment on the optoelectronic properties of the CdTe/CdS junction.

1. Introduction

Commercial development of photovoltaic systems requires a technology which is reliable, efficient and most importantly low cost. Of the potential photovoltaic technologies which could achieve this, thin film CdTe/CdS photovoltaic devices satisfy all the requirements. Current predictions for this material are: (i) module efficiencies in excess of 15% [1], (ii) CdTe/CdS thin film technology will have lower cost manufacturing compared to silicon technologies at around 1 ECU per W_p [2], and (iii) the energy payback time is significantly lower for CdTe/CdS devices compared to other technologies [3]. Thin film CdTe/CdS photovoltaic devices are therefore excellent contenders for commercial development. Progress has been made in improving the efficiency of CdTe/CdS research devices with 16.0% obtained in 1997 [4]. The alternative CIS thin film photovoltaic has achieved slightly higher efficiencies than CdTe [5]. However, estimates of energy pay back times for CIS indicate that it is comparable to or slightly higher than for amorphous silicon [6]. Best estimates indicate possible pay back times of less than one year for thin film CdTe modules [7]. The issue of the toxicity of Cd has received attention in recent years. At 10% efficiency, 10 MW_p of CdTe modules require about 3 tonnes of Cd [8]. The hazard presented by CdTe is unknown as most studies are projections based on the toxicity of Cd and other Cd compounds [9]. Studies have shown CdTe to be more toxic than CIS [10], but have also shown that leaching of Cd from broken modules does not exceed the contamination limits on drinking water [11]. Clearly the safety issues for both manufacture and use of CdTe modules need to be well considered before large scale deployment. This is all set in context by remembering that the current annual world production of free Cd is 2×10^4 tonnes, much of which will eventually find its way into the environment as free Cd.

However, the rate at which efficiency gains are reported has slowed down in recent years. In contrast to these results the predicted theoretical efficiency is 29.7% [12]. Much of the improvement achieved to date has been through optimization of device fabrication and processing without a detailed understanding of the optoelectronic properties of these devices. Much is known about the changes in the microstructure of these polycrystalline materials as a result of changes in the growth and post-growth processing conditions. The $CdCl_2$ treatment has long been known to improve the efficiency of these devices. Numerous studies have shown that it results in changes in crystal texture, grain size and orientation, strain and defect distribution have all been studied [13]. What is much less clear are the changes in the optoelectronic properties which relate directly to the device efficiency. The aim of this work is to probe the changes in the optoelectronic properties of these devices using PL which directly probes the optically active centers which will be relevant to the photovoltaic response of these device structures. Numerous studies of device characteristics have been reported in the literature involving measurements of parameters such as V_{OC}, J_{SC}, FF, η, I–V response, spectral response, capacitance measurements and deep level transient spectroscopy (DLTS). These studies, when related to device growth and processing have been of value as they have allowed the optimization of the device structures as far as can be achieved using an empirical approach. They do not, however, identify which specific active impurity centers in the device are responsible for the increase in efficiency nor are they able to obtain detailed information about the distribution of such centers throughout the device. In order to drive the efficiency of these devices higher the optoelectronic properties must be studied in detail and related to the PV device efficiency.

We have used low temperature photoluminescence spectroscopy to study the distribution of the active optoelectronic centers throughout thin film CdTe solar cell devices. When combined with the studies referred to above, this gives a more complete picture of the centers responsible for limiting the efficiency of these devices.

2. Experimental

The solar cells were provided by ANTEC GmbH and consisted of a 2 mm thick glass superstrate with a 100 nm layer of SnO_2. Onto this an 80 nm layer of CdS was deposited by close space sublimation (CSS) and finally a 8 μm layer of CdTe, also grown by CSS. The post-growth $CdCl_2$ treatment and bevel etching were performed in our laboratory. The back CdTe surface of each cell was coated with $CdCl_2$ by evaporation and then heated in air at 400 °C for 10, 20, 30, 40, 60 and 120 min. The cells were then polished with 0.25 μm diamond paste to remove surface morphology before being chemically bevelled in a bromine-methanol mixture. The gradient of the bevel etch and depth of CdTe remaining after polishing were profiled using a Tencor instruments Alpha-Step 200 profiler and had typical gradients of 1:1000. The photoluminescence measurements were performed by exciting with the 457.9 nm line of an Argon ion laser. The beam was focused to a 250 μm diameter spot on the samples. The samples were mounted in a 10 K closed-cycle helium cryostat which was mounted on an x-y-z stage, allowing the laser spot to be moved along the bevel, exciting luminescence in the CdTe at different depths into the sample from the back CdTe surface to the front CdTe/CdS interface. Spectra were recorded using a grating monochromator coupled to a cooled photodiode array. Front surface PL excited through the glass was also performed on the samples. The depth resolution of the luminescence profile is determined by the size of the focused laser spot, the absorption coefficient of CdTe and the minority carrier diffusion length. Based on available data, we can estimate this to be 0.25–0.5 μm. Preliminary time-resolved luminescence studies have shown lifetimes varying from 0.1–0.4 ns in these structures.

3. Results and discussion

The cell characteristics following the anneal have been discussed previously [14] and are summarized in Table I.

The effect of the $CdCl_2$ treatment is to increase the photovoltaic conversion efficiency of the cell which results from an increase in the open circuit voltage (V_{OC}), short circuit current (J_{SC}) and the fill factor (FF). These changes are accompanied by metallurgical effects. These include a reduction in the strain with the formation of sub-grain boundaries. Although grain growth is known to occur in some samples, it is not observed in these samples which have larger, $\sim 1\,\mu m$, grains before the $CdCl_2$ treatment [15] as grain growth is favored in samples with smaller (sub-micrometer) grains. Analysis of the I–V characteristics also shows a decrease in interface recombination states and a change in the dominant current transport mechanism from tunneling to thermally activated transport [16]. It should be noted that this current transport change is not always observed [17]. The $CdCl_2$ treatment is also known to induce a type conversion in the CdTe from n-type, as-grown, to p-type through the formation of chlorine A centers which act as acceptors with an energy 125 meV above the valence band edge [18].

Fig. 1a shows a comparison of the PL spectra taken from the as-grown sample compared with the 10 min annealed sample (Fig. 1b to 1d). A comparison of Fig. 1b to 1d shows the evolution of the PL spectra as a function of depth through the CdTe layer. Fig. 2 shows a 3D plot of the PL spectra which illustrates the changes which occur in the PL emission from different positions in the CdTe layer. These changes result from the $CdCl_2$ anneal as described above. In the treated sample, a broad peak at 1.38 eV is visible at the back surface (Fig. 1b), due to a donor–acceptor pair (DAP) recombination between a cadmium vacancy complex and a shallow chlorine donor [19]. This peak is notably absent from the back surface PL of the untreated sample (Fig. 1a). Also visible at the back surface of the treated sample is a sharper peak at

TABLE I Electrical characteristics of cells

Anneal (min)	V_{OC}(V)	J_{SC}(mA cm^{-2})	FF	η (%)
As grown	0.55	13	31	2.1
10	0.70	22	57	8.4
20	0.72	21	51	7.9
30	0.67	18	53	6.6
40	0.64	20	53	6.7
60	0.62	19	50	6.0

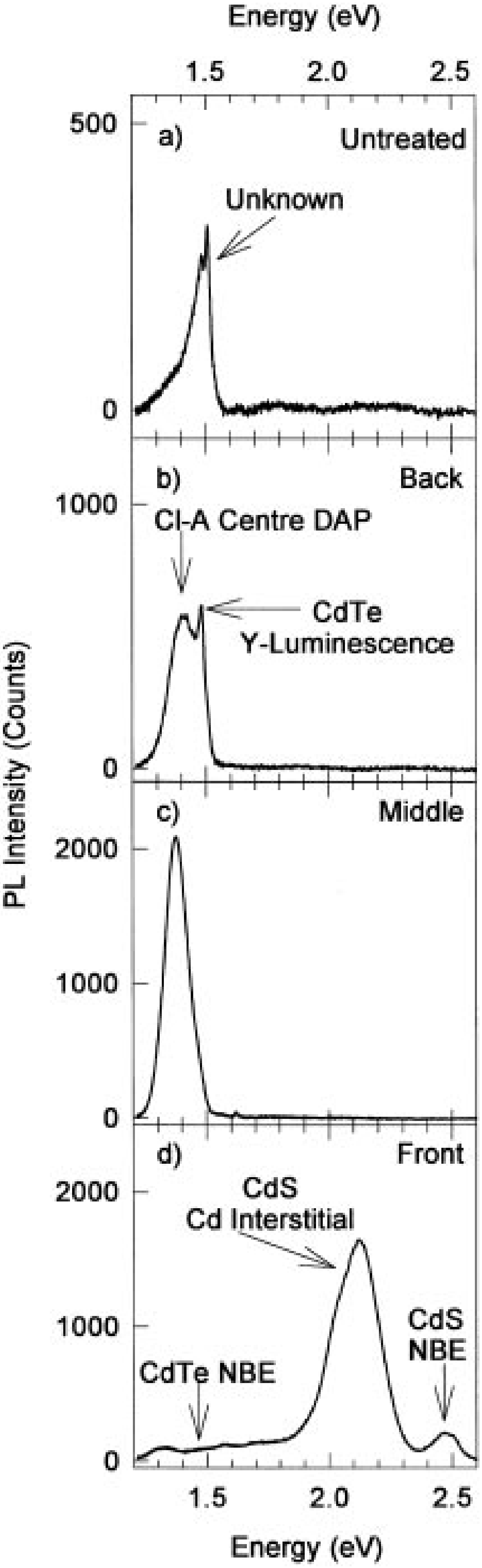

Figure 1 Low temperature PL spectra (a) from back of untreated sample, (b) from back CdTe surface of 10 min treated sample, (c) middle of 10 min treated sample and (d) front CdTe/CdS interface region.

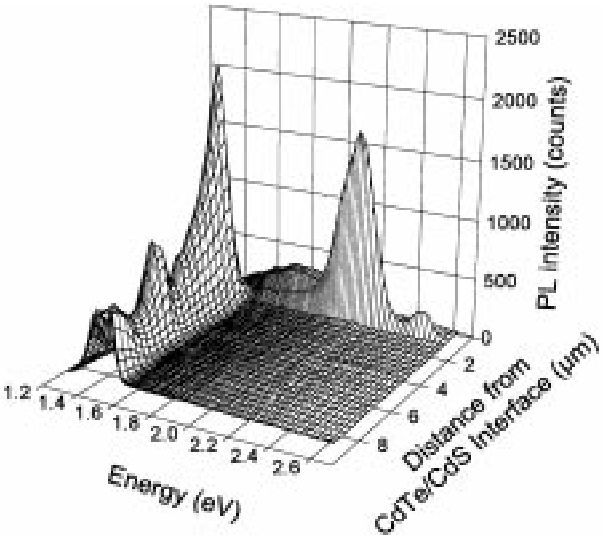

Figure 2 PL spectra as a function of energy and depth through the CdTe layer.

1.475 eV, which corresponds to the *Y* luminescence due to Te dislocations induced by the polishing of samples prior to the chemical etching [20, 21]. This peak disappears at 1–2 µm or more below the surface of the sample, and is not present in samples which were not polished prior to etching (not shown). The samples are polished to remove surface morphology and give smoother bevels with improved depth resolution. A study of the effects of the back surface polishing will be published elsewhere [22]. In all samples, near band edge emission in the region of 1.6 eV was either absent or very small compared to deeper level emissions. The work done by Figueroa *et al.* [23] and Halliday *et al.* [24] associates this with large grain sizes, high defect densities and short carrier lifetimes. In some of the samples, most notably those annealed for 10, 20 and 40 min, the 1.38 eV peak is observed to smoothly shift to lower energies as the CdS layer is approached. This is due to sulfur diffusion from the CdS layer, causing a mixed region of CdTe/CdS which is known to have a bandgap lower than the CdTe bandgap. There is a broad feature from 1.6–1.8 eV visible in the CdS in Fig. 2 and also Fig. 1d. This may be due to Te complexes in the CdS [25].

Fig. 3 shows the positions of the PL peaks as a function of depth through the CdTe layer. Following the work of Ohata *et al.* [26] and Pal *et al.* [27] the bandgap of the mixture CdS_xTe_{1-x} follows the empirical formula:

$$E_g(CdS_xTe_{1-x}) = kx^2 + (E_g(CdS) - E_g(CdTe) - k)x + E_g(CdTe)$$

The solid solution has a minimum bandgap at $x = 0.25$ which is 80 meV below the CdTe bandgap at 10 K. If $k = 1.7$ eV from Pal *et al.* [27] then the molar fraction x of sulfur in the CdTe can be estimated based on the shift to lower energies of the 1.38 eV peak, assuming that it is entirely due to sulfur diffusion. This gives a range of sulfur diffusion profiles, which are shown in Fig. 4. Sulfur diffusion was not observed in the untreated sample, although a sharp change in the PL spectra of this sample at a depth of about 5 µm into the CdTe was

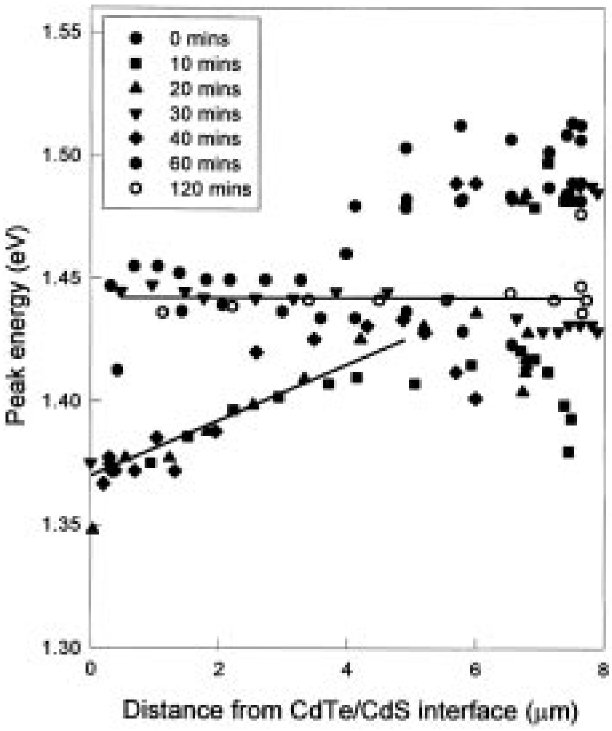

Figure 3 PL peak position as a function of position through CdTe layer for samples annealed at different times. The lines show the shift which occurs in the 10, 20, 40 min and the 120 min samples and are discussed in the text.

observed. The origin of this change is unknown. In the samples with long annealing times (60 and 120 min) the smooth shifting of the PL peak position associated with sulfur diffusion is not observed. This can be ascribed to an even distribution of sulfur throughout the CdTe layer. If it is assumed that the entirety of the sulfur has diffused evenly throughout the cell (which provides a limiting scenario) then the shift in energy due to sulfur diffusion can be calculated to be 0.01 eV. A study of diffusion in polycrystalline CdTe/CdS thin films obtained a diffusion constant of $4 \times 10^{-14}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$ at similar annealing temperatures and also indicated rapid diffusion of S along grain boundaries [28]. This is consistent with our observation of a fairly uniform S profile in the 60 and 120 min samples which have relatively large grains. All the samples exhibited a peak at 2.12 eV close to the CdTe/CdS interface. This is thought to be due to Cd interstitials [29] in the CdS layer. This is further supported by the observation that the 2.12 eV peak exists only in the interface region and does not extend into the unaffected CdS region. The 2.58 eV peak observed in some samples may be near band edge CdS emission which agrees well with the low temperature bandgap of CdS [30].

Fig. 5 shows the total integrated PL intensity of each sample as a function of depth through the CdTe layer. As can be seen, the more efficient samples (10, 20, 40 min) show the greatest intensity approaching the CdS/CdTe interface. This change in PL intensity is indicative of a reduction in non-radiative recombination routes in the near-interface region, possibly due to the effects of the sulfur diffusion as discussed above. A correlation can be seen between Figs 4 and 5. The samples with longer anneal times (60, 120 min) show a shift in the region of maximum intensity towards the back surface of the device, suggesting that non-radiative recombination centers are no longer preferentially passivated near the CdS/CdTe interface. The 30 min sample is anomalous and does not fit the behavior of the other samples.

Fig. 6 shows the observed electroluminescence spectra from the first four samples. The untreated

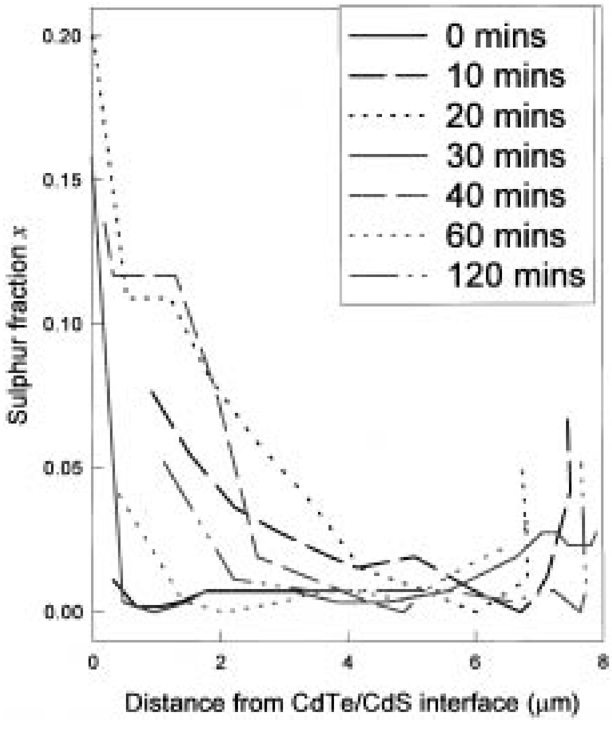

Figure 4 Fraction x of sulfur concentration in CdTe layer as a function of position through CdTe layer for samples annealed at different times. The fraction x is determined using the expression in the text.

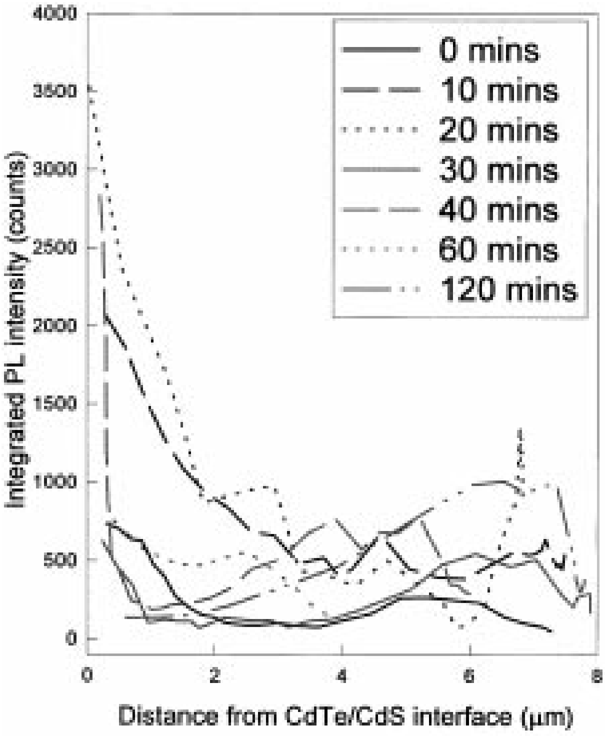

Figure 5 Integrated PL intensity as a function of distance through CdTe layer for samples annealed at different times.

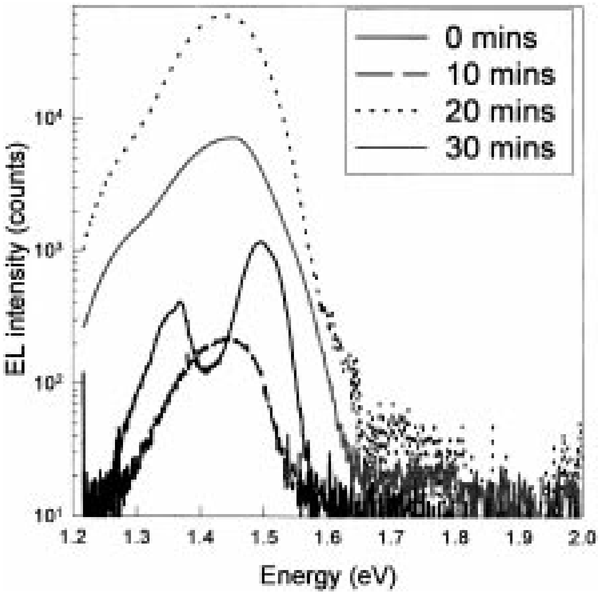

Figure 6 Electroluminescence emission from samples annealed for 0, 10, 20 and 30 min.

sample has a distinctive spectrum consisting of two peaks at 1.476 eV and 1.36 eV. In the $CdCl_2$-treated samples there is only a single peak visible at 1.43 eV. Work done by Ferrer and Salvador [31] finds room temperature EL peaks from polycrystalline CdS at 1.61 eV and 1.35 eV due to sulfur vacancy-free hole recombination and sulfur vacancy-cadmium vacancy DAP recombination, respectively. It is possible that the peaks we observe are related to these peaks but shifted towards each other due to the influence of the CdTe and CdS intermixing and the bandgap increase due to being at 10 K. This will be further complicated by the presence of vacancy complexes. It is also possible that the observed 1.476 eV peak in the untreated sample was *Y* luminescence caused by structural defects in the CdTe near the interface [21]. After $CdCl_2$ treatment the two peaks combine completely. No electroluminescence was observed in the samples with annealing times greater than 30 min, suggesting that excess $CdCl_2$ treatment renders the centers responsible for electroluminescence inactive. The intensity behavior of the EL with anneal time is not understood, however, both the PL, and particularly the EL, intensity correlate with V_{OC} in these structures.

4. Conclusions

The sulfur diffusion profile for $CdCl_2$-annealed CdTe/CdS solar cells has been quantitatively estimated from the shift in PL energy levels. Increased sulfur diffusion gradients correspond to regions of lower non-radiative recombination center density as we approach the CdS/CdTe interface through the CdTe. This also corresponds to a maximum cell efficiency of 8.4% with an anneal time of approximately 10 min in air at 400 °C. The 1.48 eV *Y* luminescence peak is only visible near the back surface of the samples and is thought to be associated with dislocations induced by polishing the samples. Lack of near band edge emission suggests the samples have large grains with high defect densities which correlated with the observed PL spectrum which is dominated by deep level emissions.

Acknowledgments

We acknowledge ANTEC GmbH for provision of the solar cell samples. M. D. G. Potter and M. Cousins acknowledge EPSRC for studentships. This work has been supported by the EU under contract number JOR3980218.

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Received 22 March
and accepted 26 June 2000