

Interface energetics and engineering of Cu(In,Ga)Se₂ solar cells

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The electronic properties of the photovoltaically active interface in thin film polycrystalline, heterojunction solar cells can be controlled by binding tailor-made ligands at the surface of the absorber, followed by chemical bath deposition of the window semiconductor. We show experimental results for the free surface of single crystals of absorbers and for actual cell structures. The results can be explained by improved band line-up, higher band bending or both.

1. INTRODUCTION

Probably the major problem in optimizing thin film polycrystalline electronic devices is that of finding conditions for minimal current and voltage loss across the grain surfaces and interfaces. This is easy to understand as losses of this type will scale in one way or the other with the surface and interface areas, areas that will increase with decreasing grain size. Just increasing the grain size is fine, as long as it does not run counter to the idea behind polycrystalline devices, which often is simplicity and keeping down the cost of their fabrication. Interface optimization has therefore long been an active area of research with considerable successes, in the case of the leading thin film cells, the CdTe and CuInSe₂ - based ones (cf. for example, ref. 1).

Thus we could show several years ago that the hitherto mysterious affect of air annealing on CuInSe₂ - based cells can be ascribed, first and foremost to a rather simple defect chemical reaction involving Se vacancies [2]. This explanation was found to be of general validity for most chalcogenide semiconductors [3]. According to it, reaction with molecular oxygen decreases the free

electron concentration in the bulk of the grains, passivates positively charged surface defects, potential electron traps and recombination centres and probably provides the first layer for a rather stable oxide layer in the case of CuInSe₂.

In further work, using electrochemical methods, we could show that the surface of CuInSe₂ is extremely responsive to the redox conditions of the contacting electrolyte showing continuous shifts of over 1 V in the flat band potential, i.e. in the band edge positions [4]. This then suggest the use of modified chemical oxidants to be able to fine tune the position of the flat band potential. As a result we embarked on a program to explore the use of tailor - made molecular ligands, that will bind chemically to the semiconductor surface and have an additional functional group that serves to tune the shift in band edge position, i.e. in electron affinity [5]. Choice of ligands was dictated by a number of requirements, viz.

- chemical bonding to the semiconductor surface (i.e. chemisorption, rather than physisorption);

- ability to attach additional groups to impart desired functionalities, that can be varied (to allow us to observe trends) and
- ability to withstand conditions necessary for deposition of additional conducting phase.

In the case of CuInSe_2 and related materials, we looked for groups that can bind to In in an oxide environment, because of the known In oxide nature of this surface. In addition this bond had to be resistant to rupture in the reducing environment used for the chemical bath deposition of the CdS window onto the absorber in this cell.

2. EXPERIMENTAL

Ligand synthesis will be described elsewhere [Moav et al. to be published]. Thin polycrystalline films of Cu(In,Ga)Se_2 (CIGSe) were prepared by 3-source physical evaporation as described elsewhere [6].

Their mode of binding to semiconductor surfaces was elucidated using FT-IR according to earlier described procedures [5, 7].

The effects of ligand binding to the free surface was followed by Contact Potential Difference (CPD) measurements, using the Kelvin probe technique, to obtain work function, electron affinity and band bending changes with respect to untreated surfaces [5, 7].

CdS window layers were deposited using chemical bath deposition from a standard ammonia bath. We tried to ascertain that the deposition did not affect ligand binding, using FT-IR. Quite unexpectedly we found that organic or amine residues remain at the interface between absorber and window after chemical bath deposition. This makes it difficult to determine unequivocally the presence of ligands at the interface. Such experiments were carried out using minimal thickness (< 10 nm) CdS.

Au contacts were deposited by vacuum evaporation.

Electrical measurements were made using an HP 4155 semiconductor parameter analyzer.

3. RESULTS AND DISCUSSION

In our earlier work we showed that benzoic acids on CuInSe_2 (and CdTe [7], CdSe [8] and GaAs [to be published]), change the semiconductor's electron affinity in a manner that roughly scales with the dipole moment of the substituted benzene ring part of the molecule. With the partial exception of GaAs binding those ligands to the semiconductor surface did not affect their band bending at the free surface. Therefore we looked for ligands that might have stronger effects, both in terms of binding and electrically. In particular we were interested in ligands that, upon binding might induce some electron transfer between the surface *cum* adsorbed ligand and the semiconductor's space charge layer. In this way we arrived a dicarboxylic acids and cyclic disulfides as binding groups. The effects of the latter will be reported elsewhere (Bruening et al., submitted for publication; cf. also [9]). Here we concentrate on the effects of the dicarboxylic acids.

Chemical binding was deduced from changes in the FT-IR spectra after exposure of the semiconductor to a solution of ligand. CdTe rather than CuInSe_2 crystals were used for this because of the still rather high defect density in the latter which makes them opaque in the relevant IR regions.

CPD measurements (on CdTe) showed changes in work function (up to 400 mV), largest for nitrile (CN-) substituted ligands and smallest for methoxy (OCH₃-) substituted ones, i.e. similar to what was observed earlier with the simpler ligands. In this case, however, in contrast to earlier, part of those changes was due to changes in band bending. If the semiconductor surface was treated with the solvent only, 600 mV band bending was found. Exposure to CN-substituted ligands changed this to 230 mV, while exposure to methoxy substituted ligands led to a change in

band bending to 460 mV. We explain this tentatively using a simple molecular orbital picture, involving the HOMO of the ligand and presumed surface states on the semiconductor, similar to earlier ideas (cf. for example ref. 10).

In the next step we applied the ligands to polycrystalline thin films of Cu(In,Ga)Se₂ of photovoltaic cell quality [11], and followed this by CdS chemical bath deposition and Au evaporation. The I-V characteristics of the resulting device structures were measured (cf. Fig. 1). From the figure it is clear that devices made with films to which the CN-substituted ligand was bound, yield I-V characteristics that are superior to those obtained with OCH₃-substituted ones. This result, which could be reproduced with different batches of absorber films, represents the first clear-cut evidence that it is possible to use molecules at a hidden interface to influence charge transport through a solar cell. The reasons for this behaviour can be one or more of the following:

- better band line-up; however this is not very likely as earlier we measured the band line up of this type of cell and found no spike and a very small positive conduction band discontinuity [12];
- higher built-in voltage (difference in measured open-circuit voltage between CN- and OCH₃- treatments from 370 to 470 mV); this awaits the results from experiments that repeat the earlier ones on CdTe. If these can be taken as guideline then this explanation is also unlikely as the opposite effect was observed at the free surface;
- decrease in surface recombination velocity; experiments to try to probe this directly are planned.

4. CONCLUSIONS

We have shown that molecular treatments can be used to affect charge transport properties of Cu(In,Ga)Se₂ - based thin film polycrystalline photovoltaic devices. We

stress that these effects are observed, notwithstanding the fact that it is quite certain that the molecules do not form a continuous layer, separating the CdS window from the (In,Ga)Se₂ absorber. This means that in this case, in contrast to most other uses of molecules on semiconductors, internal short-circuiting is not a problem. This is so because the effect of the molecules is not so much to affect charge transport by having the charge carriers pass through them, but rather by influencing the energetics of the semiconductor interface, which they have to cross.

Acknowledgment:

This work is supported by the Israel-German Energy Research program through the KFA Jülich & the Israel Ministry of Science and the Arts, Jerusalem.

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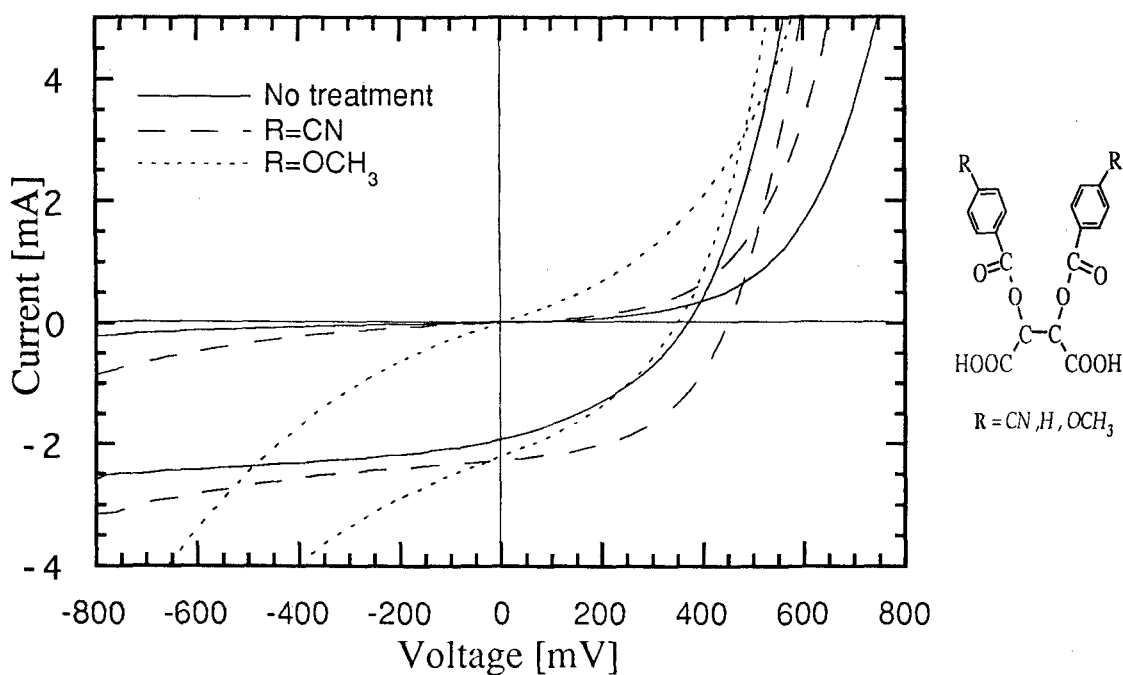


Figure 1.

Dark and photo-current - voltage characteristics of Au/CdS /CIGSe/Mo devices made without ("No treatment") and with ligand adsorption on the CIGSe prior to CdS deposition. The several mm² patch of Au blocks the ca. AM 1.5 intensity light partially.