IMPACT OF GRAIN BOUNDARIES ON THIN-FILM PHOTOVOLTAICS

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Abstract: Grain boundaries in CIGS and CdTe appear to have radically different impact on the solar-cell voltage and fill factor. The proposed explanation is that the valence-band energy in the vicinity of CIGS grain boundaries is shifted downwards, hence keeping the holes in the p-material away from the grain boundaries and potential recombination. Such grain boundaries appear to be an anomalous situation, which would not apply to CdTe and other thin-film polycrystalline materials. The suggestion to avoid grain-boundary recombination in CdTe cells is to construct a fully depleted absorber with an electron reflector layer at its rear surface.

Vpliv mej med zrni na tankoplastno fotovoltaiko

Kjučne besede: meje zrn, rekombinacije, CIGS, CdTe sončne celice

Izvleček: Meje kristalnih zrn v polikristalnih CIGS ali CdTe sončnih celicah izkazujejo popolnoma različen vpliv na napetost odprtih sponk in polnilni faktor. Članek utemeljuje razlike z razlago, da je energija valenčnega pasu v bližini mej zrn CIGSa znižana, kar zadržuje vrzeli v p-materialu proč od mej zrn in potencialnih rekombinacij. Takšna sprememba energije valenčnega pasu izgleda neobičajna in se ne pojavlja v CdTe in ostalih polikristalnih tankoplastnih materialih. Da bi se izognili rekombinacijam na mejah zrn v CdTe je potrebno zgraditi popolnoma osiromašeno absorpcijsko plast z elektronsko odbojno plastjo za proste elektrone na zadnji strani.

1 Introduction

Thin-film polycrystalline solar cells have a typical grain, or crystallite, size the order of 1 μm. This means that approximately 1% of their atoms are located on a grain surface, and the likely possibility of extraneous electron states suggests that photovoltaic performance may be seriously compromised. In practice, however, the record-performance Cu(In,Ga)Se$_2$ (CIGS) solar cells have shown voltages very close to their crystalline counterparts, diode quality factors suggestive of minimal junction recombination, and efficiencies of near 20% /1/. In contrast, the other leading thin-film material, CdTe, has a record voltage well below that of similar band-gap crystalline cells, a diode-quality factor dominated by recombination, and an efficiency of 16.5% /2/.

If one looks at SEM cross-sections of CIGS and CdTe cells, their micron-scale structure appears remarkably similar. However, instead of the record CdTe efficiency being 3% larger than CIGS, as the two band gaps would predict, it is more than 3% smaller. This difference is dramatically illustrated in Fig. 1, where the voltage deficit for the CdTe cell is 200 mV greater than that for CIGS and the primary cause of the difference in efficiency.

The purpose of this presentation is to explore what one might expect for thin-film polycrystalline solar cells, to explain why there is such a dramatic difference between results to date with CIGS and CdTe, and suggest a strategy for eliminating that difference.

2 CIGS: the anomoly

The large voltages achieved by CIGS solar cells suggest that the grain boundaries (GB) have only a minimal effect on their voltage and fill factor. More quantitatively, one can calculate the upper limit of grain-boundary recombination velocity (S_{gb}) that would allow the voltage and fill-factor and fill-factor achieved in Ref. /1/. That value would be the order of 10^3 cm/s /3/, which would imply that only about 0.01% of the carriers entering the diode depletion region contribute to the cell's forward current through recombination. That fraction is implausibly low, especially since the comparable S_{gb} for the highest efficiency CdTe cells, and by inference other micron-scale-grain materials, must be the order of 10^6 cm/s. A possible explanation is that the carriers (holes) are blocked by an internal potential from reaching the CIGS grain boundaries.

One mechanism that might keep the holes from reaching the CIGS GBs is a positive sheet of charge at the GB. This mechanism is appealing, because the internal surfaces in p-type material may be positively charged. However, this mechanism in itself does not explain the high the voltages observed. In fact, a GB with positive charge will allow additional forward-current recombination and result in smaller voltage than for the equivalent neutral GB /3/. Physically, the same potential that assists collection by channeling the photogenerated electrons and holes will in forward bias provide channels for electrons and holes to flow in the opposite direction, allow greater recombination, increase the forward current, and hence reduce V_{OC}.

A more likely explanation for the benign nature of CIGS GBs is reduced valence-band energy in the vicinity of a
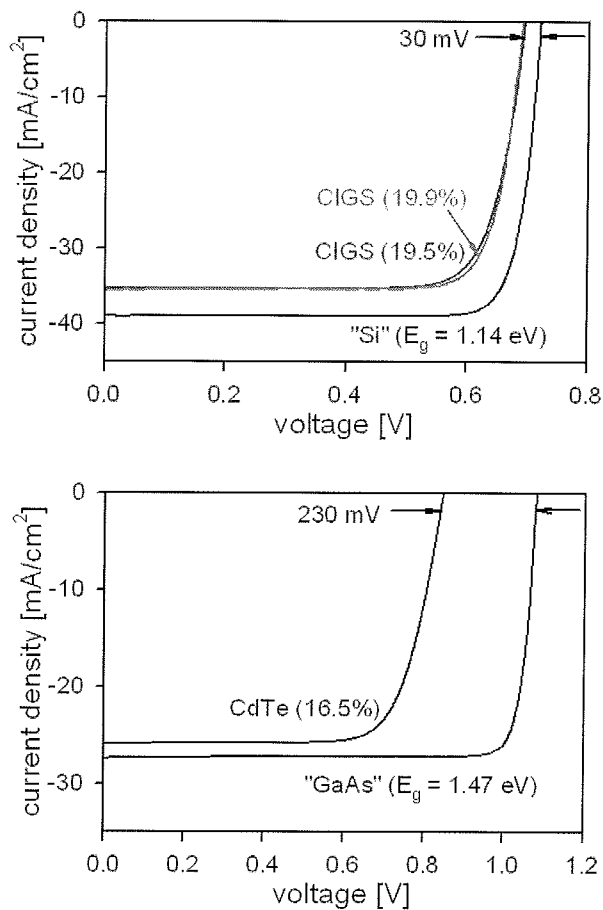
Fig. 1: Current-voltage of record-efficiency CIGS and
         CdTe cells compared to crystalline cells with
         small adjustments made for band-gap
         differences.

GB without an equivalent reduction in the conduction band
/3/. This scenario is consistent with theoretical analysis
of CIGS surfaces and interfaces, where a copper deficit
results in an expanded band gap with a lower valence band
/4/. It is also supported by experimental measurements
of copper deficiency near GBs in CIGS /5/.

Reduction in the valence band by ΔE_V near a GB and the
calculated impact on the J-V curves are shown in Fig. 2.
For S_{gb} of both 10^5 and 10^6 cm/s, the voltage and effi-
ciency should approach the values for the GB-free case
when ΔE_V is approximately 0.3 eV or larger.

The Fig. 4 curves are reasonably independent of the ΔE_V
shape or width, and they are little changed if a modest GB
charge is superimposed on the downward expansion of
the band gap. Although high voltages and efficiencies ex-
perimentally observed with CIGS solar cells could be ex-
plained by a very small value of grain-boundary recombi-
nation velocity, it seems much more likely that it is the re-
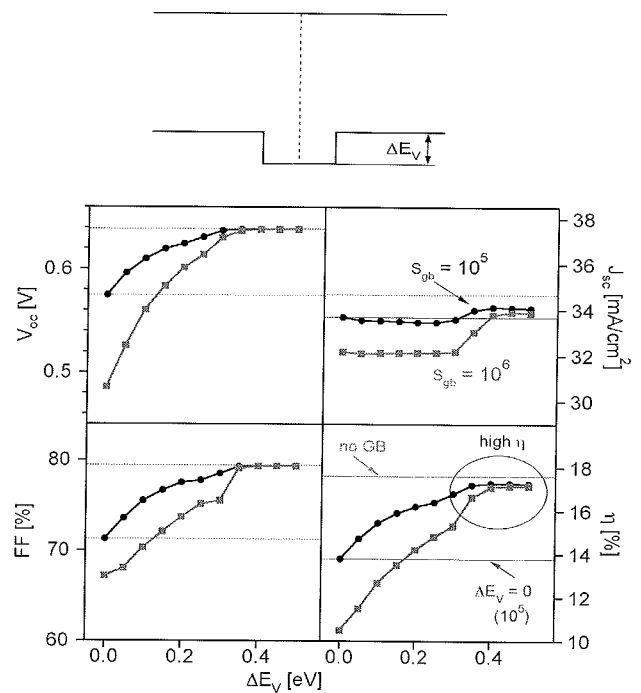sult of the band-gap expansion.

Fig. 2: Current-voltage parameters as a function of
         valence-band reduction (shown schematically
         above). The values of S_{gb} are those that would
         apply if the GB were not shielded by ΔE_V. (From
         Ref. /3/).

3 CdTe: What can be done?

If thin-film polycrystalline CdTe is the normal situation and
has a high GB recombination velocity, is there anything to
be done to improve on the voltage and efficiency that has
been achieved to date? One strategy would be to substan-
tially reduce the GB defects, increasing both hole density
and carrier lifetime (hence reducing S_{gb}), and essentially
make the thin-film CdTe similar to crystalline GaAs. This
strategy, however would require nearly a three-order-of-
magnitude increase in lifetime and two in carrier density,
essentially replicating CIGS values. Such increases are
probably not realistic.

An alternative possibility is to expand the conduction band
at the back of the CdTe layer, perhaps by alloying with Zn
or Mg, to introduce an electron reflector that keeps the
photogenerated electrons away from the back metallic
contact. This situation is illustrated in Fig. 3, where the
barrier has allowed the cell to be in larger forward bias
before the forward current limits V_{OC}.

For the electron-reflector strategy to be successful, it is
necessary for the CdTe to be fully depleted at the operat-
ing voltage so that the internal field will compensate for the
relatively low carrier lifetime. In this respect, the low carri-
er density of CdTe cells ($\sim 10^{14}$ cm^3) is advantageous, since
the depletion width at zero bias is 1 to 2 μm. To assure the
full depletion, however, it would be advisable to keep the
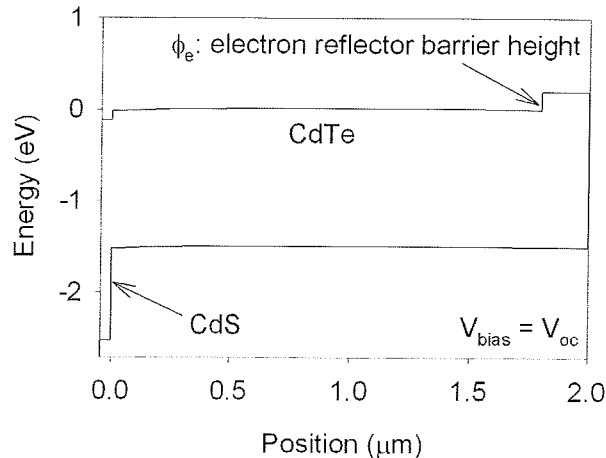CdTe-layer thickness close to 1 μm.

Fig. 3: *Schematic of electron-reflector strategy to enhance CdTe voltage and efficiency.*

Fig. 4 shows the calculated value of voltage for CdTe cells with and without the electron barrier φ_e. Without it, the voltage for cells with lifetime $\tau \sim 1$ ns is similar to that of today's high-efficiency cells. With the barrier, the voltage should approach that of crystalline material, but further improvement is not predicted for barriers much above 2 eV.
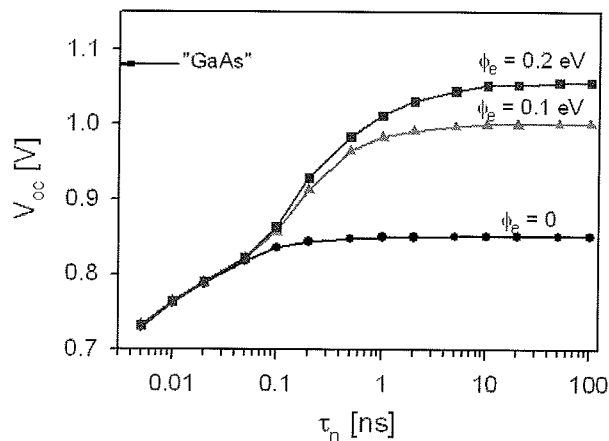

Fig. 4: *Calculated CdTe voltage as a function of electron lifetime τ and reflection-barrier height φ_e. From Ref. /6/. Full depletion is assumed.*

Although the electron-reflector structure would predict a high voltage, its fill-factor will remain lower than optimal unless the CdTe lifetime is increased somewhat above 1 ns. Nevertheless, it should be possible without the need for a major improvement in the quality of thin-film CdTe to reach one volt and 20% efficiency.

4 Conclusions

The reason for the large difference in voltage deficit, and hence efficiency, between polycrystalline CIGS and CdTe solar cells is that CIGS appears to have a fortuitous reduction in valence band near its grain boundaries that reduces the effective grain-boundary recombination velocity to 1000 cm/s or below. Polycrystalline CdTe does not have this feature, and the CdTe hole density is typically two orders of magnitude below that of CIGS. To significantly increase CdTe voltage, a different device structure based on an electron reflector at the back surface is advised.

Acknowledgments

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