

## Cadmium Telluride photovoltaics

### High efficiency for As-doped cells

Copper-doped cadmium telluride thin-film solar cells have enabled record efficiency but limited hole density and Cu diffusion mean there is little room for further improvement in device performance. Now, arsenic-doped cadmium telluride thin-films show enhanced hole density and lower dopant diffusivity leading to 20.8%-efficient solar cells.

Ken Durose

Semiconductor doping is critical to the operation of all solar cells as it creates the p-n junction that provides the built-in electric field that sweeps aside the photo-generated carriers from sunlight. Ultimately, doping is responsible for enabling both the current and voltage generation from solar cells and, in order to generate high voltages, it must supply about  $10^{16} - 10^{17}$  carriers/cm<sup>3</sup> and high minority carrier lifetimes<sup>1</sup>.

Initially, CdTe solar cells were presumed to rely on the formation of cadmium vacancies upon annealing, with the vacancies giving intrinsic acceptor doping enabling device efficiencies up to 7% in the 1970s<sup>2</sup>. However, it was not until the introduction of copper as a controlled and active p-dopant in bandgap engineered CdSeTe/CdTe devices that efficiencies were raised up to 21%<sup>3</sup>. For this kind of device, though, the maximum apparent copper doping limit of  $\sim 10^{14}$  cm<sup>-3</sup> gives little headroom for improvement. Moreover, very careful control of Cu diffusion in the absorber layer is required to guarantee the long-term stability of the devices<sup>4,5</sup>. Now, writing in Nature Energy, Wyatt Metzger and colleagues from the National Renewable Energy Laboratory and First Solar in the USA demonstrate arsenic doping of polycrystalline CdTe thin films enabling p-type carrier densities as high as  $10^{16}$  cm<sup>-3</sup> and device efficiencies up to 20.8%.<sup>6</sup>

Alternative doping approaches to copper have been explored previously, in particular using group-V elements such as N, P, As, or Sb. For instance, CdTe wafers doped with phosphorous have led to a doping density above  $10^{16}$  cm<sup>-3</sup><sup>7</sup> and a single crystal solar cell device having open-circuit voltage ( $V_{oc}$ ) = 760 mV with 8% efficiency<sup>8</sup>. For the more technologically relevant case of polycrystalline thin film CdTe PV structures, As doping by metalorganic chemical vapour deposition in conjunction with chlorine treatment has enabled 16.1%-efficient devices<sup>9,10</sup>. Recently, phosphorous-doped CdTe solar cells have achieved voltages above 1V, a landmark for CdTe, but this was limited to single-crystal devices that could not be scaled up.<sup>11</sup>

Starting from this position, Metzger and colleagues explored different ways of incorporating arsenic doping into polycrystalline thin films. They worked on doping both CdTe itself, and also thin films of the solid solution CdSeTe that is used for bandgap engineering in today's world record devices. The distributions of the arsenic dopant as revealed by spectrally resolved cathodoluminescence microscopy are shown in Figure 1. When the arsenic was introduced by post-growth in-diffusion of Cd<sub>3</sub>As<sub>2</sub> there was significant dopant segregation to the grain boundaries (Figure 1a). However, vapour transport deposition of films using pre-doped source materials generated the uniform doping profile shown in Figure 1b that is desirable for use in PV devices. This

method was used to create doped films with p-type carrier densities of  $1.5 \times 10^{16} \text{ cm}^{-3}$  and minority carrier lifetimes of 10 ns. These doping parameters enabled impressively high PV device efficiencies to be reached, with more than 100 devices having efficiencies above 19.75%. The best solar cells operate at 20.8% with  $V_{oc} = 856 \text{ mV}$ ,  $J_{sc} = 30.5 \text{ mA.cm}^{-2}$  and  $FF = 79.8\%$ , a record for a group V-doped CdTe-based device.

The paper goes on to validate the performance of the materials by comparing doped CdSeTe and CdTe devices. Both the minority carrier lifetimes and the built-in potentials of the CdSeTe doped either with copper or arsenic were comparable and high, whereas, those for CdTe doped with arsenic were lower. This indicates that the performance advantages of bandgap engineered CdSeTe could be realised equally well with either conventional copper or the emerging arsenic doping.

Nevertheless, Metzger and colleagues recognised a shortfall in  $V_{oc}$  for the As-doped devices below the value expected for the high doping level and long carrier lifetime achieved. First, their modelling results indicate that for the present doping,  $V_{oc}$  could be up to 100 mV higher if there were no interface recombination within the device, hence identifying interface recombination as a possible culprit. Grain boundary potentials were measured by Kelvin probe microscopy to be 30 mV, making them too small to cause the voltage deficit. The other factor considered was potential fluctuation caused by chemical disorder, which the researchers estimate (from cathodo- and photoluminescence linewidths) to be in the range 50 – 100 meV, this being large enough to cause the voltage shortfall. By means of optical absorption studies of the band tails in binary CdTe as a function of arsenic doping concentration, the researchers proved that the disorder was caused by the arsenic rather than by alloy fluctuations in the CdSeTe itself. Questions about arsenic doping and clustering therefore remain.

For CdTe-based devices more generally, progress towards higher efficiencies in recent years has been driven by increases in the short circuit current, which is now close to the theoretical maximum. Meanwhile the voltages achieved for polycrystalline devices have been stuck at around 850 mV for some years<sup>11</sup>. To compete with single-crystal GaAs solar cells for example, such devices need to deliver voltages that are ~80% of the bandgap value, which for CdTe is >1.15 V and slightly less for CdSeTe. Arguably increasing the  $V_{oc}$  is the last remaining research challenge for current CdSeTe/CdTe solar cells. Certainly the progress reported by Metzger and colleagues in controlled is a step in the right direction to meet this greater challenge.

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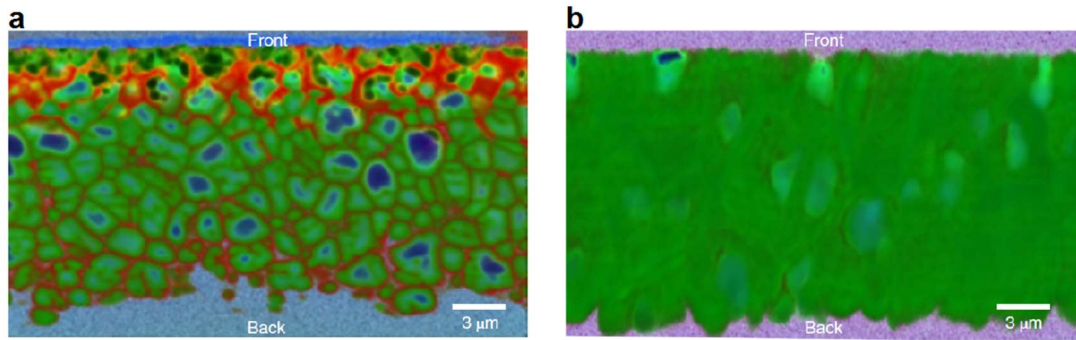


Figure 1. Cathodoluminescence images of cross-sectioned bevels of arsenic doped thin film graded gap CdSeTe solar cells. Blue indicates excitonic luminescence, green is substitutional As on Te lattice sites and red shows deeper defect transitions. **(a)** Diffusion of arsenic into the sample post-growth. **(b)** Sample fabricated via a doped source by vapour transport deposition. Compared to panel **(a)**, panel **(b)** shows a striking increase in homogeneity and the elimination of clustering that Metzger and colleagues exploited to demonstrate a high efficiency arsenic doped CdSeTe/CdTe device. The figure is reproduced from [6].