Intermediate band solar cells with AlAs-capped quantum dots

JENNA HOLDER

Jenna has recently completed her DPhil in solar energy materials, in which she worked to understand the physics of three new types if solar cells in order to aid their development. Working with solar energy was the natural result of two interests. Firstly, an interest in semiconductor technology, borne during her MPhys degree at the University of Warwick. Secondly, a passion to promote renewable energy. Jenna has actively worked with OUSU's Environment and Ethics committee to encourage more sustainable practices within the university. In her spare time, Jenna enjoys playing the piano and violin, watching films and playing squash. This article notes that intermediate band solar cells have the potential to increase solar cell efficiency. However, they have been hindered by low voltage outputs, as electrons flow out at the energy of the intermediate band, rather than the higher energy of the conduction band. Here it is shown that inserting a thin layer of aluminium arsenide (AlAs) between the intermediate band material (indium arsenide quantum dots) and the host solar cell material (gallium arsenide) can keep the voltage high and raise the solar cell efficiency. The causes for the improvement are studied, and reveal that electrical isolation of the intermediate band does not occur. Instead, the AlAs may structurally enhance the solar cell to reduce defects and electron-hole recombination.

1. Introduction

1.1 The importance of solar energy

The recent report from the intergovernmental panel on climate change states that "carbon dioxide concentrations have increased by 40% since pre-industrial times, primarily from fossil fuel emissions"[1]. The message is that the use of fossil fuels must rapidly decrease. Renewable energies, such as solar energy, are thus playing an increasingly important role in achieving a sustainable future. For solar cells to become more competitive with other electricity sources, the efficiency of converting sunlight into electricity must increase. Intermediate band solar cells are a class of solar cell that aims to address this issue.

1.2 Increasing the current - Intermediate band solar cells

To achieve a high efficiency, a solar cell must produce both a high current output and a high voltage output.

Current is produced when electrons flow from the solar cell to the external circuit. There are two steps to current generation:

1) Light hits the solar cell. The light is absorbed if it has enough energy to raise an electron from the material's valence band to the higher-energy conduction band.
2) The high energy electron will then either:
    a) fall back to the valence band to 'recombine' with the hole it left there.
    b) contribute to electric current by being swept through the conduction band to the solar cell's electrodes and into the external circuit.

It can be seen that a limiting factor to this process is the energy gap between the conduction band and the valence band (called the 'band gap'). If this band gap is too big then a high fraction of light will have an energy that is too low to be absorbed. Intermediate band solar cells combat this problem. They are made so that there is an intermediate band of energy levels between the conduction band and the valence band. This enables lower energy light to be absorbed (Figure 1) and thus can increase the electrical current output.

The voltage output is related to the energy gained by the electrons when they absorb light. To gain as much energy as possible, electrons must be extracted from the conduction band and not the lower-energy intermediate band; in other words, current produced via the intermediate band must be obtained via a two-step process ((1) and (2) of Figure 1).

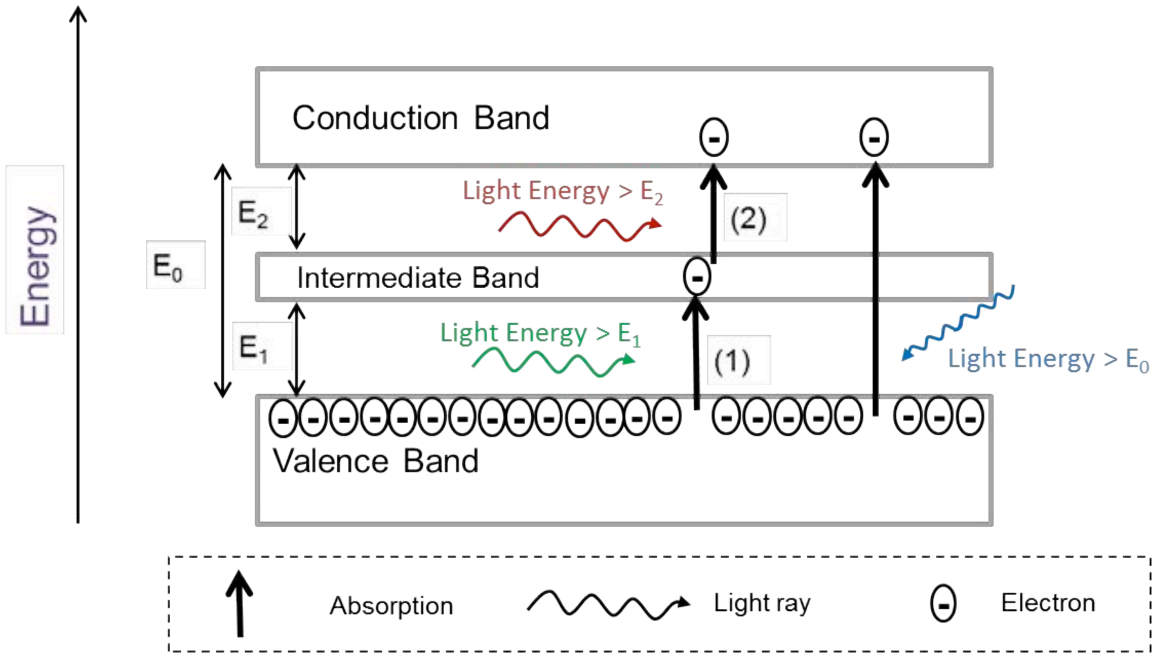


Figure 1: Energy level diagram of an intermediate band solar cell. As well as valence band - conduction band light absorption (blue light ray), light of lower energy can be used in a two-step process ((1) and (2)) to generate current.

To date, intermediate band solar cells have unfortunately had lower output voltages than standard solar cells without an intermediate band, which reduces solar cell efficiency. The low output voltages are thought to arise because energy levels form between the intermediate band and the conduction band (Figure 2A). With the assistance of heat energy[2,3] or by tunnelling[4,5] electrons can use these energy levels like a ladder. This makes it easy for electrons in the intermediate band and conduction band to mix and for the bands to become indistinct from each other. In other words, the conduction band energy is 'pinned' to the energy of the intermediate band, which limits the output voltage of the solar cell to the difference in voltage between the valence band and intermediate.

In 2000[6], Marti et al, proposed a solution to mitigate this voltage reduction: they used layers of quantum dots to form the intermediate band. Quantum dots are materials that are smaller than a material-dependent threshold, termed the Bohr radius, which is usually on the order of nanometres. They are useful because they only have a few energy levels, unlike the continuum of levels in a conduction band or valence band. Thus, when energy levels in these quantum dots merge together to form the intermediate energy band, the band can be electronically separate from the energy bands of the host material (Figure 2B). Due to the ease of processing, most quantum dot intermediate band solar cells (QD IBSCs) are made of indium arsenide quantum dots (InAs QDs) – whose high-energy levels form the intermediate band embedded in a gallium arsenide (GaAs) solar cell – whose energy levels form the valence and conduction bands.

Despite the quantum dots, ladder levels are still present, so output voltages continue to be low. These ladder levels have been determined to be from indium gallium arsenide (InGaAs), which forms when indium from the InAs quantum dots mixes with the gallium from the GaAs. This intermixing occurs to reduce the strain that arises between the InAs and GaAs crystal lattices during solar cell fabrication[7].

1.3 Increasing the voltage – aluminium arsenide layers

The solution proposed here is to insert aluminium arsenide (AlAs) between the InAs QDs and the GaAs layers. The AlAs could restore a high output voltage via two potential means. Firstly, it has been seen to prevent the intermixing of indium and gallium at the quantum dot edge[8,9], which would prevent the formation of InGaAs ladder levels. Secondly, it has a much wider band gap than the rest of the solar cell: AlAs has a band gap of 2.16 eV[10], whereas that of GaAs is 1.42 eV[10] and that of the InAs QDs is about 1.1 eV. The proposed band diagram is shown in Figure 2C. The wide band gap of AlAs might present an electronic barrier to electrons[4,11], isolating the intermediate band.

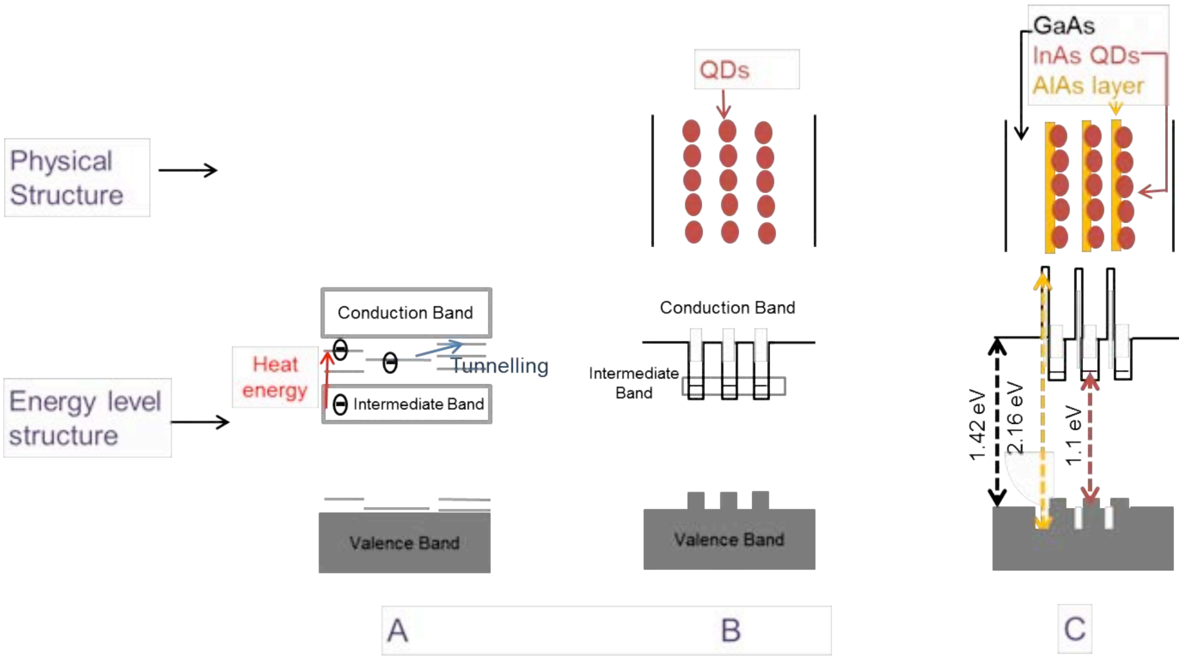


Figure 2: A) Energy level structure of intermediate band solar cell with ladder levels (grey lines), enabling electrons to escape to the conduction band with the help of heat or tunnelling. B) Physical and energy level structure of quantum dots (QDs) within a solar cell, forming an intermediate band between the conduction band and valence band. C) InAs QDs covered with wide band gap AlAs in a GaAs solar cell.

This report will study the changes induced by the AlAs layer in three steps:

1. Identify whether there are any 'ladder states' between the intermediate band and conduction band

2. Examine the mechanism of charge extraction from the intermediate band: if heat or tunnelling help the charges

from the quantum dots to escape to the GaAs bands then the energy bands are still mixed.

3. Examine the rate and means of charge recombination in the cell, as the output voltage is affected by these.

2. Devices

Two devices were constructed for this study by Mr. Frank Tutu of University College London. The first was a reference InAs QD/ GaAs device termed the 'control cell' and the second was the 'AlAs cell', which was identical to the control cell other than the inclusion of 2 monolayers (~0.57 nm) of AlAs on each quantum dot layer. The structure of the devices is illustrated in figure 3. The

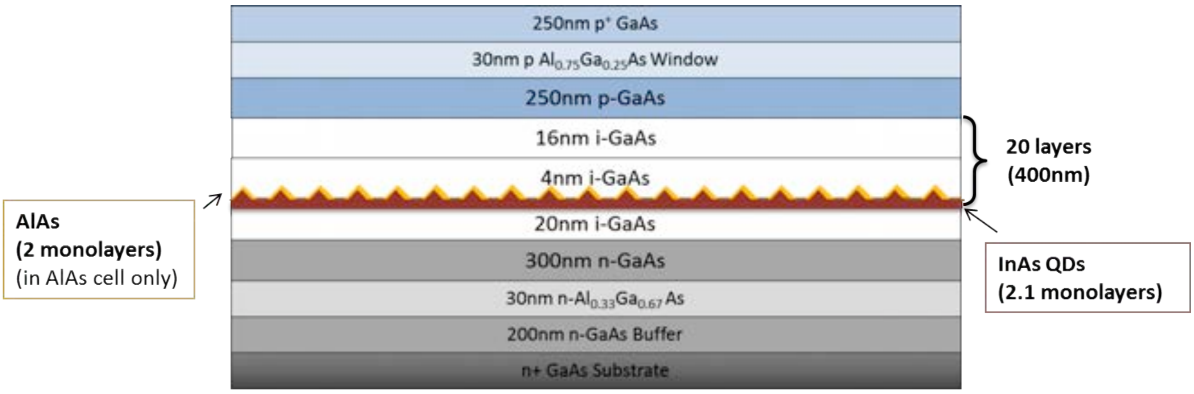


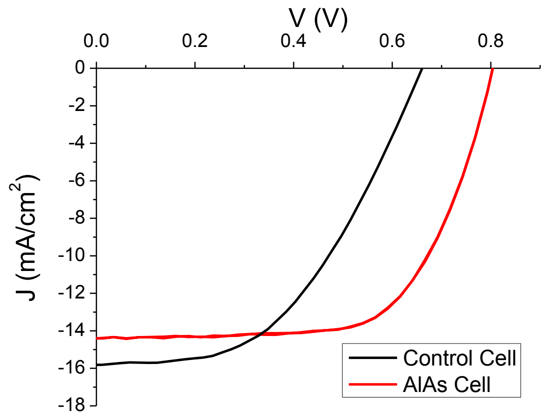
Figure 3: Device structure, giving thicknesses, doping information and the position of the AlAs layer in the case of the AlAs cell.

blue layers are p-doped (more positively charged than intrinsic gallium arsenide). The white layers are denoted with the letter 'i' for intrinsic gallium arsenide. The grey layers are n-doped (more negatively charged than intrinsic gallium arsenide). This 'p-i-n' structure is required to create an electric field across the solar cell, which drives charges towards the correct electrodes.

3. Results

3.1 Solar cell performance

Measurements of current density (J) vs voltage (V) taken under mid-latitude solar illumination provide key solar cell efficiency parameters. The results for the two solar cells are shown in Figure 4.



	Control	AlAs
J_{sc} (mA/cm^2)	15.70	14.35
V_{oc} (V)	0.66	0.80
Fill Factor (%)	48	58
Power conversion efficiency (%)	5.1	6.6

Figure 4: Current Density – Voltage (JV) curves at AM 1.5 illumination for the control cell and the AlAs cell. The table gives the efficiency parameters, as explained in the text.

Pertaining to the current output and voltage output are, respectively, the J_{sc} (short circuit current density) and V_{OC} (open circuit voltage). J_{sc} is the output current when there is no load connected to the solar cell and the voltage is zero. V_{OC} is the voltage across a solar cell when no current is flowing. Strikingly, V_{OC} is much higher for the AlAs cell than that of the control cell. The fill factor, which is a measure of the curve's 'squareness', is also increased, indicating more favourable resistance through the AlAs cell. These two factors result in a higher power conversion efficiency for the AlAs cell than the control cell. Unfortunately, the AlAs layer is detrimental to the J_{sc}.

3.2 Ladder Levels

Electroreflectance is used to identify the energies of electronic transitions (electrons moving from lower to higher energy levels). Electronic transitions appear as oscillations in the spectrum. Therefore, the presence of ladder levels would be identified by an oscillation at energies corresponding to the difference in valence band and ladder level energies.

Comparing the spectra of the control cell with the AlAs cell (figure 5A), the main electronic transition in both devices is at

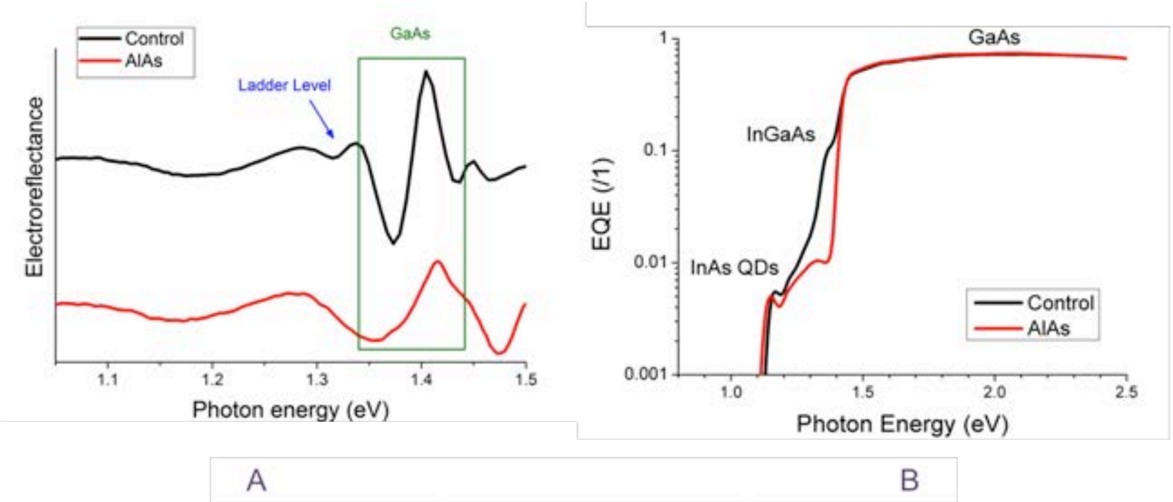


Figure 5: Electroreflectance (A) and external quantum efficiency (B) for the control cell and the AlAs cell

around 1.4 eV, which is the GaAs valence band to conduction band transition (shown in the green rectangle). The other main feature to note is at around 1.33 eV in the control cell spectrum, likely to originate from valence band to InGaAs ladder level transitions. The lack of this InGaAs feature in the AlAs cell spectrum supports the hypothesis that AlAs has reduced indium/gallium intermixing.

A negative effect of these reduced InGaAs levels is shown in the external quantum efficiency (EQE) spectra (Figure 5B), which identify which electronic transitions contribute to the short-circuit current. In both devices, current from GaAs transitions is seen at energies greater than 1.4 eV and the valence band to InAs QD transition is seen below 1.2 eV. However, the AlAs cell outputs significantly lower current in the InGaAs ladder level region (1.2 - 1.4 eV), which explains the lower J_{sc}.

3.3 Charge extraction from the intermediate band

With fewer InGaAs ladder levels, it should be harder for electrons to get from the intermediate band to the conduction band via heat or tunnelling. Instead, secondary light would be required to excite an electron to the conduction band[12] (step (2) of Figure 1). This secondary photon must raise the electron from the intermediate band to the conduction band before it can fall back to the valence band and recombines with a hole (timescale of the order of 1ns[13]). The likelihood of this 'two photon to one electron' process occurring in this timeframe increases with greater intensity of light, so the current output from the QD intermediate band should increase superlinearly with increasing light intensity. The current output as function of incident light intensity was recorded to test this. Two light energies were used, representing different electronic transitions in the solar cell: 1.38 eV - GaAs valence band to conduction band - and 1.16 eV - valence band to InAs QD intermediate band.

Figure 6 reveals that the current increases linearly with light intensity for both electronic transitions, which is characteristic of one photon producing one electron. In other words, despite the reduction in ladder levels, the intermediate band is not isolated from the conduction band, as secondary light raise electrons from the QD intermediate band to the conduction band.

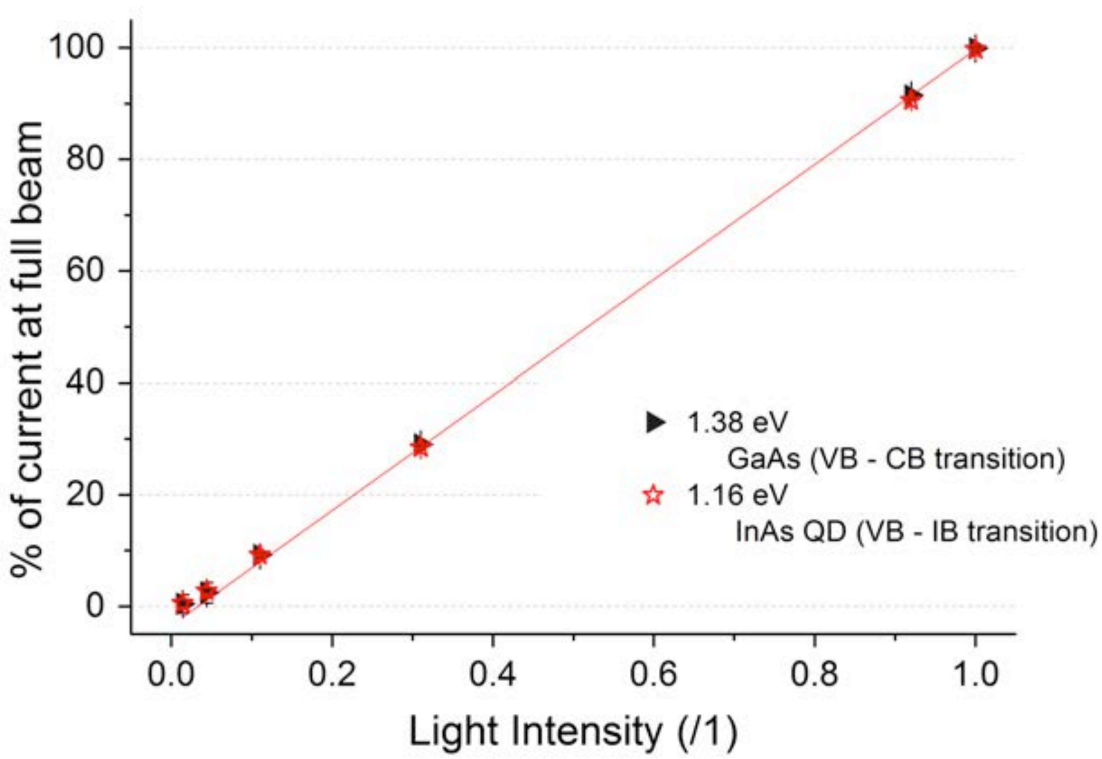


Figure 6: Current output on exposure of the cell to light of energies: 1.38 eV (exciting the valence band to conduction band transition) and 1.16 eV (exciting the valence band to intermediate band transition). Values are shown as a percentage of current output at full light intensity.

To determine whether it is heat that promotes the electrons, external quantum efficiency of the QD transitions from the AlAs cell was measured as a function of temperature (Figure 7). Current is seen from the QDs even at the lowest temperature of 102K (-171°C). There is a small rise in QD current up to 202K (-71°C) and then a drop in current at higher temperatures. Other measurements attributed this drop to an increase in charge recombination as temperatures rise past 202K (data not shown). If the charge extraction process was purely thermal, a more dramatic rise in EQE would be expected from 102K – 202K as well as a low quantum dot current at 102K[5].

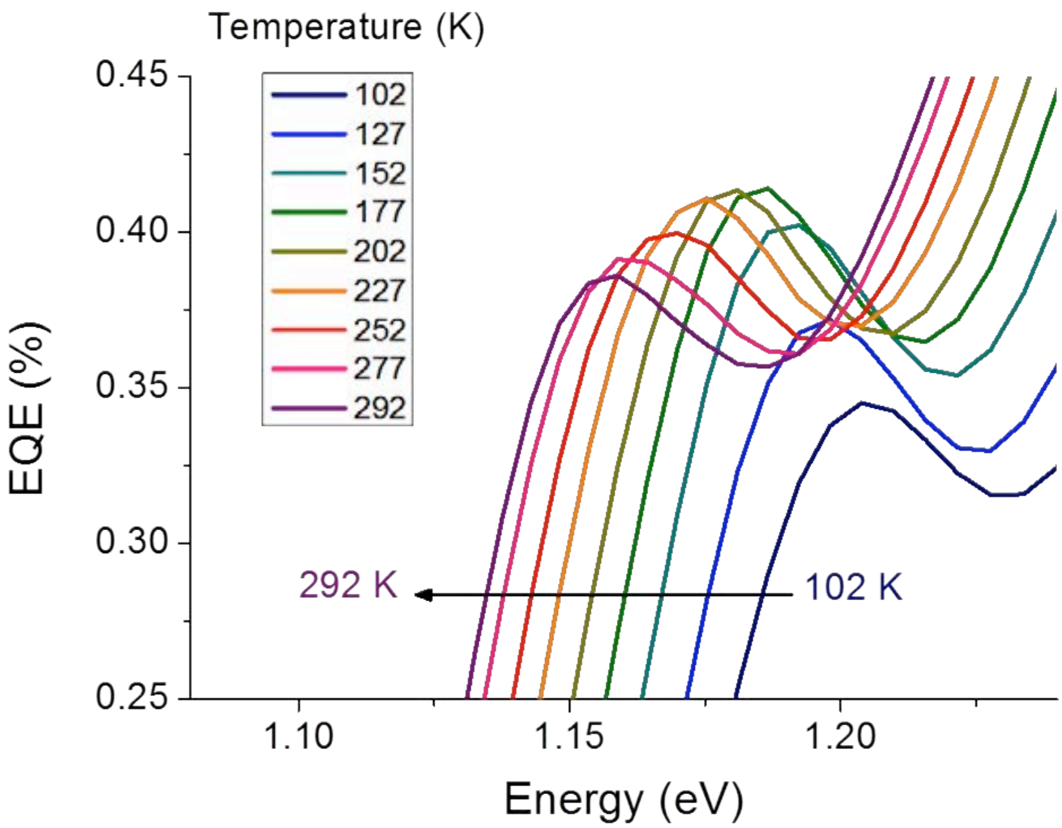


Figure 7: External quantum efficiency (EQE) around the QD excitation.

As both light and heat do not have a key role in exciting electrons from the intermediate band in the AlAs device, tunnelling must prevail. This is feasible according to other studies in the literature with thin layers (< 15 nm) between QDs[5,14]. Analysis of photoluminescence data (not shown) showed moderate tunnelling in both the AlAs and the control devices, but the AlAs cell showed a slightly higher hindrance to tunnelling movement of charges.

As the AlAs does not isolate the intermediate band from the conduction band, the investigation into the higher open circuit voltage now turns to the examination of charge recombination in the solar cell.

3.4 Charge Recombination

V_{OC} is voltage that causes charge generation to balance charge recombination[15,16] and thus cause a net current of zero.

- Charge generation: absorption of light generates free electrons in the conduction band and leaves their opposite charge ("holes") in the valence band.
- Charge recombination: at forward voltage, electrons and holes are injected into the solar cell from the electrodes. These move across the solar cell in the opposite direction to the photogenerated electrons and holes and recombine with the photogenerated holes and electrons (respectively). Therefore, these injected charges create a recombination current, acting in the opposite direction to the generation current.

A higher rate of recombination will result in a lower forward voltage being required to balance generation current, i.e. the V_{OC} will be lower. To study *just* the recombination current, current-voltage measurements were taken in the dark (Figure 8).

The AlAs cell starts injecting at a higher forward voltage than the control cell, i.e. there is initially a lower injection rate. As electrons can tunnel through the AlAs, it seems unlikely that the AlAs barrier can reduce charge injection. Alternatively, something about the AlAs cell could limit recombination. By fitting the dark JV curve to the diode equation, parameters can be extracted that quantify any recombination differences.

These parameters are the ideality factor (n) and reverse saturation current density (J_0). The higher the ideality factor, the more ways there are for electrons and holes to recombine. J_0 gives the magnitude of this recombination. These parameters are related to the V_{OC} by equation 1, where J_{ph} is the photogenerated current density, q is the charge on an electron and k_B is Boltzmann's constant.

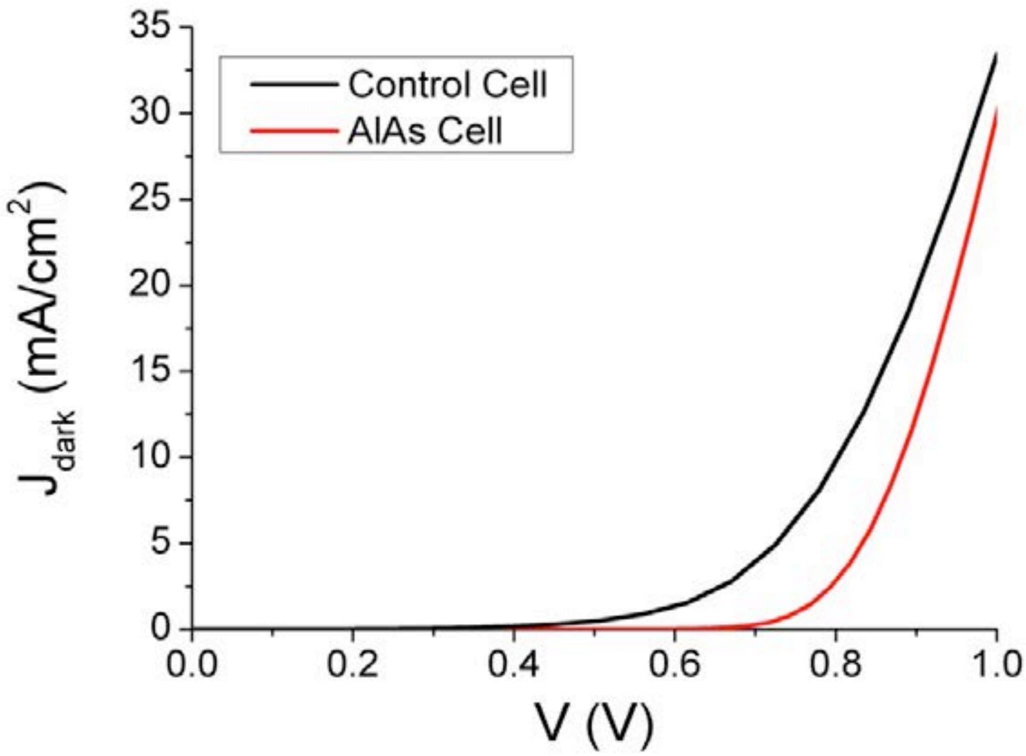


Figure 8: Dark JV curves of the control cell (black) and AlAs cell (red).

$$V_{OC} = \frac{nk_BT}{q}\ln\left(\frac{J_{ph}}{J_0} + 1\right)$$

Equation 1

The parameters extracted from the dark JV curves are shown in Table 1. The ideality factor of 1.46 for the AlAs cell is

Cell	N	J_0 (mA/cm^2)
Control	3.74 ± 0.10	(2.4 ± 0.1) E-3
AlAs	1.46 ± 0.06	(5.3 ± 1.2) E-9

Table 1: Dark JV parameters for the AlAs and control solar cells.

comparable to other GaAs solar cells[17]. However, the much higher value for the control cell may be a sign of recombination via dislocations[17], increasing with the density of defects in the solar cell[18]. Defects are known to form when strain builds up in the device[19–21]. Supporting this theory is the six-orders of magnitude higher J_0 for the control cell compared to the AlAs cell, which is again is a possible indicator of defects[17,22,23].

The lower J_0 and n for the AlAs cell indicate decreased recombination in this device, which would lower the injection rate as seen in the dark JV curves and reduce V_{OC}. The reason for the improved recombination may be that the AlAs layer results in fewer defects within the device, or that the lack of InGaAs states help to reduce recombination.

4. Conclusions

AlAs layers were incorporated into InAs quantum dot/GaAs solar cells to try to isolate the QD intermediate energy band from the GaAs conduction and valence bands. It was hoped isolation would be achieved for two reasons: firstly, AlAs is a wide band gap material, and secondly, placing AlAs between InAs and GaAs will reduce indium-gallium intermixing. The aim of this was to increase the open-circuit voltage, and indeed it increased from 0.66 V to 0.80 V, but this was at the expense of the short-circuit current. Electroreflectance and external quantum efficiency measurements showed that the reduction in short-circuit current arose from fewer InGaAs ladder levels in the AlAs cell, so the AlAs successfully prevented the intermixing of gallium and indium.

The increase in open-circuit voltage was not due to the isolation of the intermediate band. This would have been demonstrated by light causing the transition from the QD intermediate band to the GaAs conduction band. Instead, tunnelling is the dominant extraction mechanism, showing that the AlAs barrier does not prevent charge movement from the QDs. Dark current-voltage measurements showed that the open-circuit voltage improves in the AlAs cell because of reduced recombination, possibly due to fewer defects in the AlAs cell.

REFERENCES

1. IPCC. *IPCC Fifth Report - Mitigation of Climate Change.* (2014). at <http://www.ipcc.ch/report/ar5/wg3/>
2. Linares, P. G. *et al.* Voltage recovery in intermediate band solar cells. *Sol. Energy Mater. Sol. Cells* **98,** 240–244 (2012).
3. Luque, A. *et al.* Radiative thermal escape in intermediate band solar cells. *AIP Adv.* **1,** 022125 (2011).
4. Antolín, E. *et al.* Advances in Quantum Dot Intermediate Band Solar Cells. *IEEE* 65–70 (2010).
5. Antolín, E. *et al.* Reducing carrier escape in the InAs/GaAs quantum dot intermediate band solar cell. *J. Appl. Phys.* **108,** 064513 (2010).
6. Marti, A., Cuadra, L. & Luque, A. Quantum dot intermediate band solar cell. *Conf. Rec. Twenty-Eighth IEEE Photovolt. Spec. Conf. - 2000 (Cat. No.00CH37036)* 940–943 (2000). doi:10.1109/PVSC.2000.916039
7. Eisele, H. *et al.* Change of InAs/GaAs quantum dot shape and composition during capping. *J. Appl. Phys.* **104,** 124301 (2008).
8. Arzberger, M., Käsberger, U., Böhm, G. & Abstreiter, G. Influence of a thin AlAs cap layer on optical properties of self-assembled InAs/GaAs quantum dots. *Appl. Phys. Lett.* **75,** 3968 (1999).
9. Hu, D., McPheeters, C. C., Yu, E. T. & Schaadt, D. M. Improvement of performance of InAs quantum dot solar cell by inserting thin AlAs layers. *Nanoscale Res. Lett.* **6,** 83 (2011).
10. Adachi, S. GaAs, AlAs, and AlxGa1−xAs Material parameters for use in research and device applications. *J. Appl. Phys.* **58,** R1 (1985).
11. Song, H. Z. *et al.* AlGaAs capping effect on InAs quantum dots self-assembled on GaAs. *Phys. Lett. A* **375,** 3517–3520 (2011).
12. Cuadra, L., Marti, A. & Luque, A. Present status of intermediate band solar cell research. *Thin Solid Films* **451-452,** 593–599 (2004).
13. Dawson, P. *et al.* Relaxation and recombination in InAs quantum dots. *Phys. Status Solidi* **244,** 2803–2815 (2007).

14. Mazur, Y. I. *et al.* Interdot carrier transfer in asymmetric bilayer InAs⁄GaAs quantum dot structures. *Appl. Phys. Lett.* **86,** 063102 (2005).
15. Ruppel, W. & Wurfel, P. Upper limit for the conversion of solar energy. *IEEE Trans. Electron Devices* **27,** 877–882 (1980).
16. Luque, A., Martí, A. & Stanley, C. Understanding intermediate-band solar cells. *Nat. Photonics* **6,** 146–152 (2012).
17. Hubbard, S. M. *et al.* Effect of strain compensation on quantum dot enhanced GaAs solar cells. *Appl. Phys. Lett.* **92,** 123512 (2008).
18. Breitenstein, O., Altermatt, P. P., Ramspeck, K. & Schenk, A. The Origin of Ideality Factors n > 2 of Shunts and Surfaces in the Dark I-V Curves of Si Solar Cells. *Proc. 21st Eur. PVSEC, Dresden* 625–628 (2006).
19. Alonso-Álvarez, D. *et al.* Carrier recombination effects in strain compensated quantum dot stacks embedded in solar cells. *Appl. Phys. Lett.* **93,** 123114 (2008).
20. Tutu, F. K. *et al.* Improved performance of multilayer InAs/GaAs quantum-dot solar cells using a high-growth-temperature GaAs spacer layer. *J. Appl. Phys.* **111,** 046101 (2012).
21. Ng, J. T., Bangert, U. & Missous, M. Formation and role of defects in stacked large binary InAs/GaAs quantum dot structures. *Semicond. Sci. Technol.* **22,** 80–85 (2007).
22. Wei, G. & Forrest, S. R. Intermediate-Band Solar Cells Employing Quantum Dots Embedded in an Energy Fence Barrier. *Nano Lett.* **7,** 218–222 (2007).
23. Lu, H. F. *et al.* Temperature dependence of dark current properties of InGaAs/GaAs quantum dot solar cells. *Appl. Phys. Lett.* **98,** 183509 (2011).