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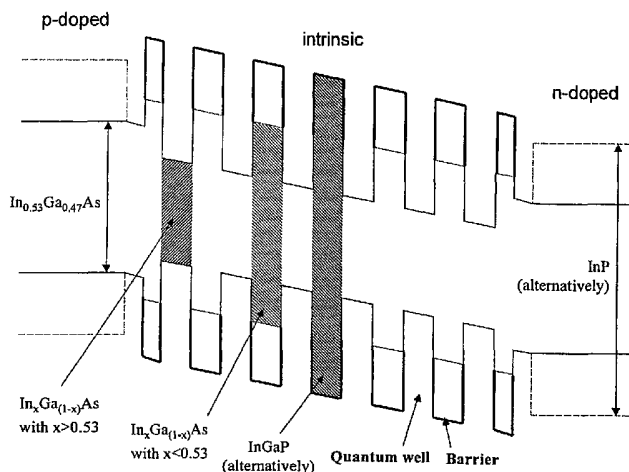
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(54) Title: PHOTOVOLTAIC DEVICE HAVING AN INGAAS/INGAP MULTIPLE QUANTUM WELL PORTION



(57) Abstract: A photovoltaic cell to convert low energy photons is described, consisting of a p-i-n diode with a strain-balanced multi-quantum-well system incorporated in the intrinsic region. The bandgap of the quantum wells is lower than that of the lattice-matched material, while the barriers have a much higher bandgap. Hence the absorption can be extended to longer wavelengths, while maintaining a low dark current as a result of the higher barriers. This leads to greatly improved conversion efficiencies, particularly for low energy photons from low temperature sources. This can be achieved by strain-balancing the quantum wells and barriers, where each individual layer is below the critical thickness and the strain is compensated by quantum wells and barriers being strained in opposite directions minimising the stress. The absorption can be further extended to longer wavelengths by introducing a strain-relaxed layer (virtual substrate) between the substrate and the active cell.



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PHOTOVOLTAIC DEVICE HAVING AN
INGAAS/INGAP MULTIPLE QUANTUM WELL PORTION

This invention relates to an improved photovoltaic device/cell for the conversion of heat radiation into electricity.

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Thermophotovoltaics (TPV) is the use of photovoltaic (PV) cells to convert heat radiation, e.g. from the combustion of fossil fuels or biomass, into electricity. The energy spectrum is often reshaped using selective emitters which absorb the heat and re-emit in a narrow band. The re-emitted radiation may be efficiently converted to electric power using a PV cell of appropriate low band-gap. Higher PV cell efficiencies can be achieved by introducing multi-quantum-wells (MQW) into the intrinsic region of a p-i-n diode if the gain in short-circuit current exceeds the loss in open-circuit voltage [K.W.J. Barnham and G. Duggan, J. Appl. Phys. 67, 3490 (1990). K. Barnham et al., Applied Surface Science 113/114, 722 (1997). K. Barnham, International Published Patent Application WO-A-93/08606 and U.S. Patent US-A-5,496,415 (1993)]. A Quantum Well Cell (QWC) in the quaternary system InGaAsP lattice-matched to InP substrates is a promising candidate for TPV applications as the effective band-gap can be tuned, out to about 1.65 μm ($\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$), without introducing strain, by varying the well depth and width, to match a given spectrum. The enhancement in output voltage of a QWC is a major advantage for TPV applications [P. Griffin et al., Solar Energy Materials and Solar Cells 50, 213 (1998). C. Rohr et al., in Thermophotovoltaic Generation of Electricity: Fourth NREL Conf., Vol.460 of AIP Conf. Proc. (American Institute of Physics, Woodbury, New York, 1999), pp.83-92].

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There is considerable interest in extending the absorption to longer wavelengths for higher overall system efficiencies with lower temperature sources; and lower temperature fossil sources have also lower levels of pollution. Appropriate and inexpensive substrates of the required lattice constant and band-gap are not available, so the lower band-gap material is often strained to the substrate, introducing dislocations which increase non-radiative recombination. Freundlich et al. have proposed strained quantum well devices [U.S. Patent US-A-5,851,310 (1998), U.S. Patent US-A-6,150,604 (2000)], but these can only incorporate a restricted number of wells without creating dislocations. Freundlich proposes limiting the number of wells

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to a maximum of 20, which will not produce sufficient absorption for efficient generation however. In a MQW system, these dislocations can be reduced by strain-balancing the layers; alternating barriers and wells have bigger and smaller lattice-constants, but on average are lattice-matched to the substrate [N.J. Ekins-Daukes et al., Appl.Phys.Lett.75, 4195 (1999)].

Viewed from one aspect the invention provides a photovoltaic device having a multiple quantum well portion formed of strained alternating quantum well layers of $\text{In}_x\text{Ga}_{1-x}\text{As}$, where $x > 0.53$, and barrier layers of $\text{Ga}_y\text{In}_{1-y}\text{P}$, where $y > 0$.

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This combination of layers allows provision of an advantageously high barrier energy within the multiple quantum well system which reduces the dark current. Furthermore, this composition is well suited to stress balancing and use with the above mentioned virtual substrate.

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The above, and other objects, features and advantages of this invention will be apparent from the following detailed description of illustrative embodiments which is to be read in connection with the accompanying drawings.

20 FIG. 1 is a bandgap diagram of a strain-balanced quantum well cell. The p- and n- regions are made of material that is lattice-matched to the InP substrate, e.g. $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ or InP. The quantum wells are made of $\text{In}_x\text{Ga}_{1-x}\text{As}$ with $x > 0.53$, and the barrier of $\text{In}_x\text{Ga}_{1-x}\text{As}$ with $x < 0.53$, GaInP or InGaAsP;

25 FIG. 2 is a schematic drawing of a strain-compensated quantum well cell where the width indicates the lattice parameter of the material when unstrained;

FIG. 3 is a graph of dark current densities of a strain-balanced quantum well cell (as depicted in Figure 2 but with 30 quantum wells) compared with bulk GaSb of similar effective bandgap (see Figure 4) and lattice-matched bulk InGaAs;

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FIG. 4 is a graph of modelled internal quantum efficiency (with back-surface reflector) of a strain-balanced quantum well cell (as depicted in Figure 2 but with 30 quantum wells) compared with bulk GaSb and lattice-matched bulk InGaAs;

FIG. 5 is a graph of modelled internal quantum efficiency (with back-surface reflector) of a strain-balanced quantum well cell optimised for a Holmia emitter (not to scale);

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FIG. 6 is a graph of the dark current of an AlGaAs/GaAs quantum well cell, where the data (dots) is fitted (black line). The modelled dark current density for a QWC with a higher band-gap barrier (grey line) is reduced; and

10 FIG. 7 shows Lattice constant vs Bandgap of the material system $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{P}_y$.

A photovoltaic cell to convert low energy photons is described, consisting of a p-i-n diode with a strain-balanced multi-quantum-well system incorporated in the intrinsic region. The bandgap of the quantum wells is lower than that of the lattice-matched material, while the barriers have a much higher bandgap. The high band-gap barriers reduce the dark current. Hence the absorption can be extended to longer wavelengths, while maintaining a low dark current. This leads to greatly improved conversion efficiencies, particularly for low energy photons from low temperature sources. This can be achieved by strain-balancing the quantum wells and barriers, where each individual layer is below the critical thickness and the strain is compensated by quantum wells and barriers being strained in opposite directions. The strain is compensated by choosing the material compositions and thicknesses of the layers in such a way that the average stress is zero, taking into account the elastic properties of the materials. Thereby the creation of misfit dislocations, which are detrimental to the dark current and hence to the cell conversion efficiency, can be avoided. The number of quantum wells that can be incorporated is therefore not limited by the build-up of strain, but only by the size of the i-region, and is typically 30-60 [This is an important advantage over Freundlich's strained QWs with a maximum number of about 20 (see US-A-5,851,310 and US-A-6,150,604)]. The width of the i-region is limited by the electric field that needs to be maintained across it.

The absorption can be further extended to longer wavelengths by introducing a strain-relaxed layer (virtual substrate) between the substrate and the active cell. The device is then grown on this virtual substrate and the layers are strain-balanced with respect to the new lattice constant. This allows one to effectively move to a specific lattice

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constant which is associated with a desired band gap for the lattice matched and strain-balanced materials. This is of particular interest for thermophotovoltaic applications with lower temperature sources, as one can extend the absorption towards the required long wavelengths.

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As an example for a strain-compensated QWC, we consider a 30 well $\text{In}_{0.62}\text{Ga}_{0.38}\text{As}/\text{In}_{0.47}\text{Ga}_{0.53}\text{As}$ (InP) QWC, grown by MOVPE, whose sample description is given in Table I.

10 TABLE I: Sample description of a strain-compensated quantum well cell.

| Layers | Thickness (Å) | Material | Function | Doping | Conc. (cm^{-3}) |
|--------|---------------|---|-----------|--------|----------------------------|
| 1 | 1000 | $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ | Cap | p | $1\text{E}+19$ |
| 1 | 7000 | InP | Emitter | p | $2\text{E}+18$ |
| 30 | 120 | $\text{In}_{0.45}\text{Ga}_{0.55}\text{As}$ | Barrier | i | |
| 30 | 120 | $\text{In}_{0.62}\text{Ga}_{0.38}\text{As}$ | Well | i | |
| 1 | 120 | $\text{In}_{0.47}\text{Ga}_{0.53}\text{As}$ | Barrier | i | |
| 1 | 5000 | InP | Base | n | $1\text{E}+18$ |
| | | InP | Substrate | n | |

In FIG. 2 the strain-balancing conditions of one example are shown, where the average lattice-constant of wells and barriers is roughly the same as the InP substrate. FIG. 1 shows a schematic diagram of the energy band-gaps of this kind of structure.

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This specific sample was not designed for TPV applications; the p-region, for example, is far too thick. It does not quite fulfil the ideal strain-balanced conditions, but is close enough to avoid strain relaxation as is evident by the low dark current of the device (see FIG. 3). In fact, the dark current density is even lower than in a very good lattice-matched bulk InGaAs/InP cell [N.S. Fatemi et al., in Proc. 26th IEEE PV

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specialists conf. (IEEE, USA, 1997), pp.799-804] as shown in FIG. 3. In FIG. 4 we show the spectral response (SR) (=external quantum efficiency) data of the strain-balanced QWC at zero bias. The effective band-gap, resulting from the material composition and the confinement, is about $1.77 \mu\text{m}$, which is well beyond the band-edge of lattice-matched InGaAs. Hence the strain-balanced approach has enabled the

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absorption threshold to be extended out to $1.77 \mu\text{m}$ while retaining a dark current

more appropriate to a cell with a band-edge of less than 1.65 μm . The band-edge of the strain-balanced QWC is similar to that of a GaSb cell, but it has a lower dark current (see FIG. 3). Strain-balanced QWCs in InGaP/InGaAs on GaAs have demonstrated dark currents comparable to homogenous GaAs cells [N.J. Ekins-Daukes et al., Appl.Phys.Lett.75, 4195 (1999)]. We have shown (see FIG. 3) that, if anything, $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{In}_z\text{Ga}_{1-z}\text{As}$ (InP) cells with absorption edges out to 1.77 μm have lower dark currents than bulk InGaAs cells. To obtain even lower dark currents, we need a higher band-gap in the barriers. We can achieve that by using a different material for the barrier, such as $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{P}_y$ with $y > 0$ or GaInP as indicated in FIG. 1, and an example for such a device is given in Table II.

TABLE II: Sample description of a strain-balanced quantum well cell with high bandgap barriers.

| Layers | Thickness (\AA) | Material | Function | Doping | Conc. (cm^{-3}) |
|--------|----------------------------|---|-----------|--------|----------------------------|
| 1 | 1000 | $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ | Cap | p | $1\text{E}+19$ |
| 1 | 1500 | InP | Emitter | p | $5\text{E}+18$ |
| 1 | 50 | $\text{Ga}_{0.18}\text{In}_{0.82}\text{P}$ | Barrier | i | |
| 49 | 100 | $\text{Ga}_{0.18}\text{In}_{0.82}\text{P}$ | Barrier | i | |
| 50 | 100 | $\text{In}_{0.72}\text{Ga}_{0.28}\text{As}$ | Well | i | |
| 1 | 50 | $\text{Ga}_{0.18}\text{In}_{0.82}\text{P}$ | Barrier | i | |
| 1 | 5000 | InP | Base | n | $1\text{E}+18$ |
| | | InP | Substrate | n | |

We have developed a model which calculates the SR of multi-layer $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{P}_y$ devices, lattice-matched to InP ($x = 0.47$, y) [M. Paxman et al., J.Appl.Phys.74, 614 (1993), C. Rohr et al., in Thermophotovoltaic Generation of Electricity: Fourth NREL Conf., Vol.460 of AIP Conf. Proc. (American Institute of Physics, Woodbury, New York, 1999), pp.83-92], which has been extended to estimate the SR of strain-balanced $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{In}_z\text{Ga}_{1-z}\text{As}$ on InP [C. Rohr et al., in Proc. 26th International Symposium on Compound Semiconductors No.166 in Institute of Physics Conference Series (Institute of Physics Publishing, Bristol and Philadelphia, 2000), pp.423-426]. The cell efficiency can be determined given the measured dark current data of the cell, assuming superposition of dark and light current. For photovoltaic applications

the p-region of a device would typically be as thin as 1500 Å (instead of 7000 Å) in order to increase the light level that reaches the active i-region where carrier separation is most efficient and to reduce free carrier absorption. A mirror on the back of a semi-insulating (i.e. charge neutral) substrate is particularly useful for QWCs as it enhances the well contribution significantly. The effect of such a mirror is simulated by doubling the light pass through the wells. The strain-balanced QWC is modelled with these modifications and, for the purpose of comparison, the reflectivity is removed to show the internal quantum efficiency in FIG. 4.

We compare our strain-balanced QWC as well as our lattice-matched InGaAsP QWCs with lattice-matched InGaAs monolithic interconnected modules (MIMs) [N.S. Fatemi et al., in Proc. 26th IEEE PV specialists conf. (IEEE, USA, 1997), pp.799-804], one of the best lattice-matched bulk InGaAs/InP TPV cells, and with bulk GaSb [A.W. Bett et al., in Thermophotovoltaic Generation of Electricity: Third NREL Conf., Vol.401 of AIP Conf. Proc. (American Institute of Physics, Woodbury, New York, 1997), pp. 41-53], currently the only material which is being used commercially for TPV applications. To compare efficiencies we assume 'typical' TPV conditions of 100 kW/m² normalised power density, grid shading of 5 %, and internal quantum efficiencies for all cells. A back surface reflector is an integral part of MIM technology and particularly useful for QWCs as it enhances the well contribution significantly. It also increases TPV system efficiency because longer wavelength radiation, that is not absorbed by the cell, is reflected back to the source. The efficiency projections for various illuminating spectra are calculated from data presented in FIGs. 3 and 4 and are summarised in Table III. The relative efficiencies are rather more reliable than the absolute values.

TABLE III: Comparison of predicted efficiencies (in %) of bulk InGaAs MIM, GaSb, lattice-matched and strain-balanced quantum well cells with back-mirror using internal quantum efficiencies, under various spectra at 100 kW/m², and 5% grid shading:

| Spectrum | Bulk InGaAs MIM | Bulk GaSb | InGaAsP QWC | Strain-bal. QWC |
|-------------|-----------------|-----------|-------------|-----------------|
| Solar x 100 | 16 | 16 | 20 | 19 |

| | | | | |
|--------------------|-----|-----|-----|----|
| 3200K blackbody | 18 | 18 | 22 | 27 |
| 2000K blackbody | 11 | 11 | 12 | 22 |
| 1500K blackbody | 5.5 | 5.6 | 4.8 | 14 |
| MgO | 13 | 15 | 16 | 41 |
| Ytterbia | 26 | 25 | 42 | 32 |
| Erbia | 37 | 37 | 46 | 43 |
| Holmia | 4.5 | 5.4 | 4.1 | 39 |

The lower dark current of the QWCs (see FIG. 3) is the main reason for their higher efficiencies in Table III. The lattice-matched InGaAsP QWC shows higher efficiencies than the InGaAs MIM and GaSb in all cases except for black-body temperatures below about 2000 K. Higher black-body temperatures, for example 3200 K and the solar spectrum AM1.5 (approximating 5800 K) at 100 times concentration, are favourable for the lattice-matched InGaAsP QWC. At black-body temperatures around 2000 K and below, the strain-balanced QWC outperforms the others. Particularly with the MgO emitter, which was designed for a GaSb cell [L. Ferguson and L. Fraas, in Thermophotovoltaic Generation of Electricity: Third NREL Conference Vol.401 of AIP Conf. Proc. (American Institute of Physics, Woodbury, New York, 1997), pp. 169-179], the strain-balanced QWC is significantly better and shows an efficiency which is about 50 % higher than that of a GaSb cell (see Table III).

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Based on these results it should be possible to use this concept of strain-balanced QWCs to extend the absorption threshold even further, beyond 2 μm , optimised for TPV applications with a Holmia emitter (see FIG. 5). The efficiency for such a strain-balanced QWC with a Holmia emitter [M.F. Rose et al., Journal of Propulsion and Power 12, 83 (1996)] is predicted to reach 39 % under the same conditions as discussed above. The more the band-edge of a PV cell is extended towards longer wavelengths, the more suitable it becomes for lower temperature sources.

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The conversion efficiency can be further substantially increased by reducing the dark current. In strain-balanced devices, this can be achieved if higher band-gap material is used for the barriers as indicated in FIG. 1 and Table II.

5 A model for the dark current behaviour of QWCs is used in FIG. 6. In FIG. 6, a dark current density of an AlGaAs/GaAs quantum well cell is fitted, and it shows that the modelled dark current density for a QWC with a higher band-gap barrier is reduced and hence the efficiency will be increased.

10 In order to be lattice-matched to an InP substrate, the material composition of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{P}_y$ must be chosen to lie on the vertical line in FIG. 7 going through InP, which corresponds to $x \approx 0.53 + 0.47 y$. That means, the lowest bandgap one can achieve with lattice-matched material is with $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$, a bandgap of $E_g \approx 0.74$ eV. Strain-compensation in a multi-layer system allows one to achieve lower effective
15 band-gaps. The quantum wells are compressively strain, going down the branch from $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ towards InAs (i.e. $x > 0.53$), and to compensate the barriers have tensile strain going up the branch from $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}$ towards GaAs (i.e. $x < 0.53$). To improve the dark current with higher bandgap barriers one can use material compositions with $y > 0$ and the same lattice constant as before, i.e. going up on a
20 vertical line in FIG. 7. To achieve high bandgap barriers, these may be formed of $\text{Ga}_y\text{In}_{1-y}\text{P}$, where $y > 0$. In FIG. 7 this composition follows the upper limit between InP and GaP.

By introducing a virtual substrate, still lower bandgaps can be reached as the lattice
25 constant is increased by relaxed buffer layers. This shifts the base or reference line for strain-compensation towards the right in FIG. 7. This virtual substrate can be made of InAsP (upper branch in FIG. 7) [Wilt et al., 28th IEEE PVSC (2000), p. 1024] instead of InGaAs. Such an InAsP buffer is better in confining the dislocations in the virtual substrate, which is crucial for successfully growing a strain-compensated multi-
30 quantum well (MQW) structure on top of it.

The conditions for zero-stress strain-balance may be determined from the following considerations:

The strain ε for each layer i is defined as

$$\varepsilon_i = \frac{a_0 - a_i}{a_i}$$

where a_0 is the lattice constant of the substrate (or virtual substrate), and a_i is the
5 natural unstrained lattice constant of layer i .

A strain-balanced structure should be designed such that a single period composed of
one tensile and one compressively strained layer, exerts no shear force on its
neighbouring layers or substrate. To achieve such a zero stress situation, one needs to
10 taken into account the differences in elastic properties of the layers. Applying linear
elastic theory one can derive the following conditions

$$\varepsilon_1 t_1 A_1 a_2 + \varepsilon_2 t_2 A_2 a_1 = 0 \quad \text{(zero-stress condition)}$$

$$a_0 = \frac{t_1 A_1 a_1 a_2^2 + t_2 A_2 a_2 a_1^2}{t_1 A_1 a_2^2 + t_2 A_2 a_1^2} \quad \text{(Match substrate lattice constant)}$$

$$A = C_{11} + C_{12} - \frac{2C_{12}^2}{C_{11}} \quad \text{(Layer stiffness)}$$

20 where t_1 and t_2 are the thicknesses of layers 1 and 2, and C_{11} and C_{12} are the elastic
stiffness coefficients.

Although illustrative embodiments of the invention have been described in detail
herein with reference to the accompanying drawings, it is to be understood that the
25 invention is not limited to those precise embodiments, and that various changes and
modifications can be effected therein by one skilled in the art without departing from the
scope and spirit of the invention as defined by the appended claims.

Further examples of photovoltaic devices are given below and in the following clauses.

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A photovoltaic device having a multiple quantum well portion with alternating tensile
strained layers and compressively strained layers, said tensile strained layers and said

compressively strained layers having compositions such that a period of one tensile strained layer and one compressively strained layer exerts substantially no shear force on a neighbouring structure.

- 5 Such a device recognises that rather than seeking to provide an average lattice constant that matches the substrate, what is truly important is to balance the forces in the tensile and compressively strained layer to provide an average or effective zero stress system. A device providing an average lattice constant matching the substrate may still allow a significant build up of stress that will result in undesirable
10 dislocations.

With this concept one can extend the absorption threshold to longer wavelength without introducing dislocations.

- 15 With a strain-balanced multi-quantum-well stack in the intrinsic region of a two-terminal photovoltaic device the absorption threshold can be extended to longer wavelengths. In particular, with high bandgap barriers the dark current can be reduced at the same time, and hence the conversion efficiency is increased significantly.

- 20 What is also helpful to achieve higher conversion efficiencies is an improved voltage performance, due to a lower dark current. This is provided by the higher barriers which may also be provided when balancing the strain.

- A photovoltaic device having a multiple well quantum portion formed upon a virtual
25 substrate having a virtual substrate lattice constant different than a substrate lattice constant of an underlying substrate, wherein said virtual substrate is $\text{InP}_{1-x}\text{As}_x$, where $0 < x < 1$ and said substrate is InP.

- Using an $\text{InP}_{1-x}\text{As}_x$ based virtual substrate allows lattice matching to a quantum well
30 system having a relatively large lattice constant, and typically desirable lowbandgap.

CLAUSES

1. A photovoltaic device having a multiple quantum well portion with alternating tensile strained layers and compressively strained layers, said tensile strained layers and said compressively strained layers having compositions such that a period of one tensile strained layer and one compressively strained layer exerts substantially no shear force on a neighbouring structure.
2. A photovoltaic device as described in clause 1, wherein said neighbouring structure is one of:
a further period of one tensile strained layer and one compressively strained layer;
a layer of arbitrary doping having the same lattice constant as a substrate; and
a substrate.
3. A photovoltaic device as described in clause 1, being a crystalline photovoltaic device grown upon a substrate with a substrate lattice constant.
4. A photovoltaic device as described in clause 3, wherein at least one of said tensile strained layers or said compressively strained layers is a quantum well having a Group III/V semiconductor composition with a bandgap lower than if said quantum well had a lattice constant equal to said substrate lattice constant.
5. A photovoltaic device as described in clause 3, wherein at least one of said tensile strained layers or said compressively strained layers is a barrier having a Group III/V semiconductor composition with a bandgap higher than if said barrier had a lattice constant equal to said substrate lattice constant.
6. A photovoltaic device as described in clause 1, wherein said multiple quantum well portion is formed of alternating quantum well layers and barrier layers having a Group III/V semiconductor composition, wherein a period of one quantum well layer and one quantum barrier layer contains at least four different elements and has an average lattice constant substantially matching a neighbouring structure lattice constant.

7. A photovoltaic device as described in clause 4, wherein said substrate is InP and said compressively strained layer is $\text{In}_x\text{Ga}_{1-x}\text{As}$, where $x > 0.53$.
8. A photovoltaic device as described in clause 5, wherein said substrate is InP and said tensile strained layer is $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{P}_y$, where $y > 0$.
9. A photovoltaic device as described in clause 8, wherein $y = 1$ such that said tensile strained layer is GaInP.
10. 10. A photovoltaic device as described in clause 3, wherein said substrate is InP and said multiple quantum well portion is formed of layers of $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{Sb}_{1-y}$, where $0 \leq x \leq 1$ and $0 \leq y \leq 1$.
11. A photovoltaic device as described in clause 3, wherein said substrate is GaSb and said multiple quantum well portion is formed of layers of $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{Sb}_{1-y}$, where $0 \leq x \leq 1$ and $0 \leq y \leq 1$.
12. A photovoltaic device as described in clause 3, wherein said substrate is GaAs.
20. 13. A photovoltaic device as described in clause 12, wherein said multiple quantum well portion is formed of layers of $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$, where $0 \leq x \leq 1$ and $0 \leq y \leq 1$.
14. A photovoltaic device as described in clause 1, wherein said multiple quantum well portion is formed upon a virtual substrate composed of a strain relaxed buffer layer having a virtual substrate lattice constant different from a substrate lattice constant of an underlying substrate.
25. 15. A photovoltaic device as described in clause 14, wherein said virtual substrate is $\text{InP}_{1-y}\text{As}_y$, where $0 < y < 1$, and said substrate is InP.
30. 16. A photovoltaic device as described in clause 1, wherein said photovoltaic device is a thermophotovoltaic device.

17. A photovoltaic device as described in clause 1, wherein said quantum wells have a bandgap substantially equal to or less than 0.73eV

18. A photovoltaic device having a multiple well quantum portion formed upon a virtual substrate having a virtual substrate lattice constant different than a substrate lattice constant of an underlying substrate, wherein said virtual substrate is $\text{InP}_{1-x}\text{As}_x$, where $0 < x < 1$, and said substrate is InP.

19. A photovoltaic device as described in clause 18, wherein said multiple quantum well portion is formed with alternating tensile strained layers and compressively strained layers, said tensile strained layers and said compressively strained layers having compositions such that a period of one tensile strained layer and one compressively strained layer exerts substantially no shear force on a neighbouring structure.

15

20. A photovoltaic device as described in clause 19, wherein said neighbouring structure is one of:

a further period of one tensile strained layer and one compressively strained layer;
a layer of arbitrary doping having the same lattice constant as said virtual substrate;

20 and

said virtual substrate.

21. A photovoltaic device as described in clause 18, wherein at least one of said tensile strained layers or said compressively strained layers is a quantum well having a Group III/V semiconductor composition with a bandgap lower than if said quantum well had a lattice constant equal to said substrate lattice constant.

25

22. A photovoltaic device as described in clause 18, wherein at least one of said tensile strained layers or said compressively strained layers is a barrier having a Group III/V semiconductor composition with a bandgap higher than if said barrier had a lattice constant equal to said substrate lattice constant.

30

23. A photovoltaic device as described in clause 18, wherein said multiple quantum well portion is formed of alternating quantum well layers and barrier layers

having a Group III/V semiconductor composition, wherein a period of one quantum well layer and one quantum barrier layer contains at least four different elements and has an average lattice constant substantially matching a neighbouring structure lattice constant.

5

24. A photovoltaic device as described in clause 21, wherein said substrate is InP and said compressively strained layer is $\text{In}_x\text{Ga}_{1-x}\text{As}$, where x is larger than z of $\text{In}_z\text{Ga}_{1-z}\text{As}$ which is lattice-matched to the virtual substrate.

10

25. A photovoltaic device as described in clause 23, wherein said substrate is InP and said tensile strained layer is $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{P}_y$, where $y > 0$.

15

26. A photovoltaic device as described in clause 25, wherein $y=1$ such that said tensile strained layer is GaInP or wherein $x=1$ such that said tensile strained layer is InAsP

20

27. A photovoltaic device as described in clause 18, wherein said substrate is InP and said multiple quantum well portion is formed of layers of $\text{Al}_x\text{Ga}_{1-x}\text{As}_y\text{Sb}_{1-y}$, where $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

25

28. A photovoltaic device as described in clause 18, wherein said substrate is GaSb and said multiple quantum well portion is formed of layers of $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{Sb}_{1-y}$, where $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

30

29. A photovoltaic device as described in clause 18, wherein said substrate is GaAs.

30. A photovoltaic device as described in clause 29, wherein said multiple quantum well portion is formed of layers of $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$, where $0 \leq x \leq 1$ and $0 \leq y \leq 1$.

30

31. A photovoltaic device as described in clause 18, wherein said photovoltaic device is a thermophotovoltaic device.

32. A photovoltaic device as described in clause 18, wherein said quantum wells have a bandgap substantially equal to or less than 0.73eV

CLAIMS

1. A photovoltaic device having a multiple quantum well portion formed of strained alternating quantum well layers of $\text{In}_x\text{Ga}_{1-x}\text{As}$, where $x > 0.53$, and barrier
5 layers of $\text{Ga}_y\text{In}_{1-y}\text{P}$, where $y > 0$.
2. A photovoltaic device as claimed in claim 1, wherein said multiple quantum well portion is formed with alternating tensile strained layers and compressively strained layers, said tensile strained layers and said compressively strained layers
10 having compositions such that a period of one tensile strained layer and one compressively strained layer exerts substantially no shear force on a neighbouring structure.
3. A photovoltaic device as claimed in claim 2, wherein said neighbouring
15 structure is one of:
a further period of one tensile strained layer and one compressively strained layer;
a layer of arbitrary doping having the same lattice constant as a substrate; and
a substrate.
- 20 4. A photovoltaic device as claimed in claim 1, being a crystalline photovoltaic device grown upon a substrate layer with a substrate lattice constant.
5. A photovoltaic device as claimed in claim 4, wherein said substrate is InP.
- 25 6. A photovoltaic device as claimed in claim 1, wherein said multiple quantum well portion is formed upon a virtual substrate composed of a strain relaxed buffer layer having a virtual substrate lattice constant different from a substrate lattice constant of an underlying substrate.
- 30 7. A photovoltaic device as claimed in claim 6, wherein said virtual substrate is $\text{InP}_{1-y}\text{As}_y$, where $0 < y < 1$, and said substrate is InP.
8. A photovoltaic device as claimed in claim 1, wherein said photovoltaic device is a thermophotovoltaic device.

9. A photovoltaic device as claimed in claim 1, wherein said quantum wells have a bandgap substantially equal to or less than 0.73eV.

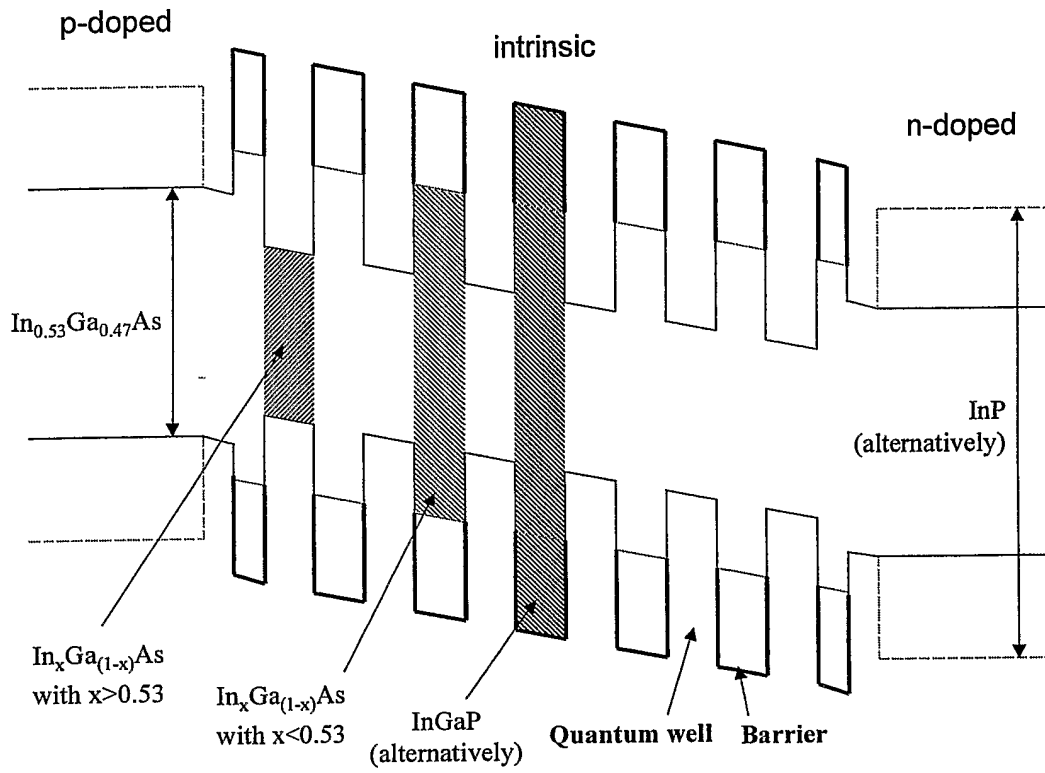


FIGURE 1

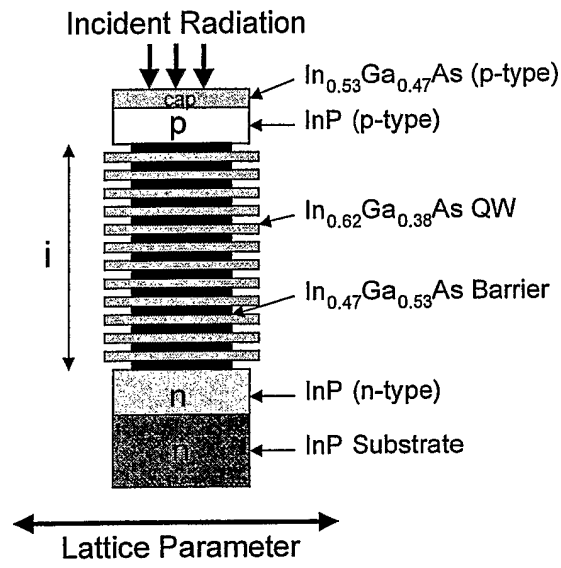


FIGURE 2

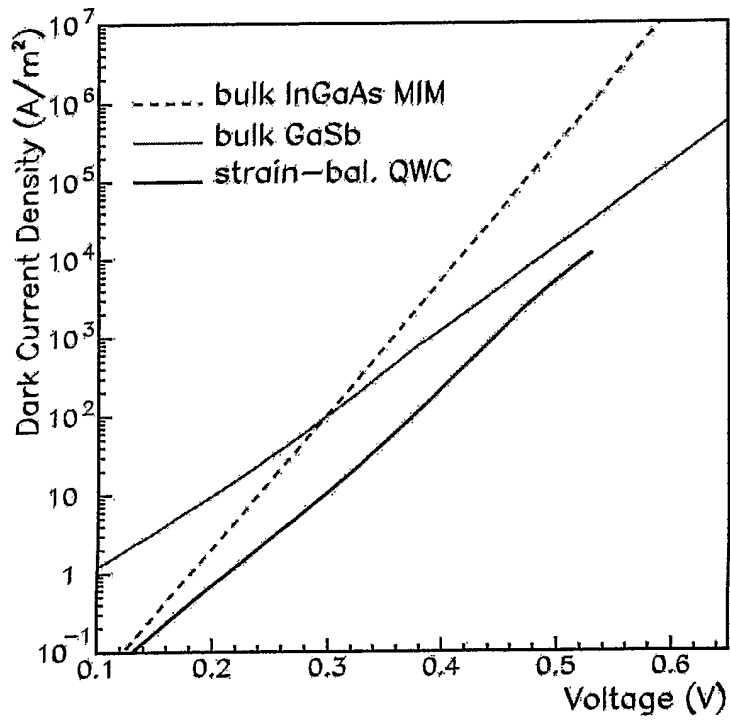


FIGURE 3

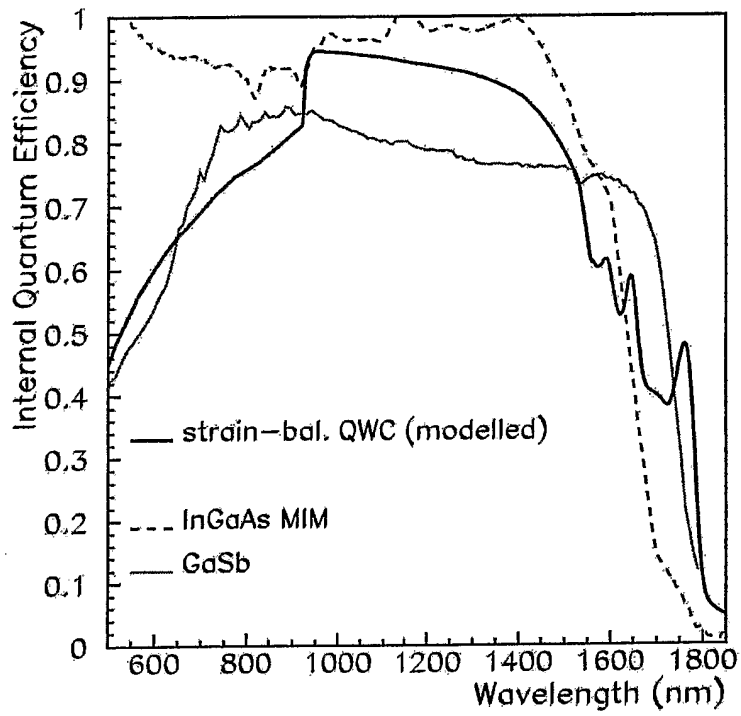


FIGURE 4

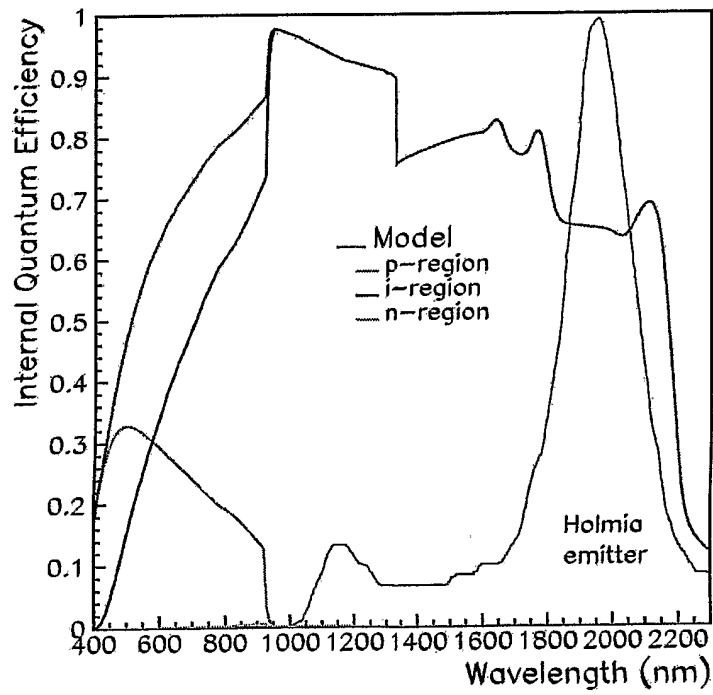


FIGURE 5

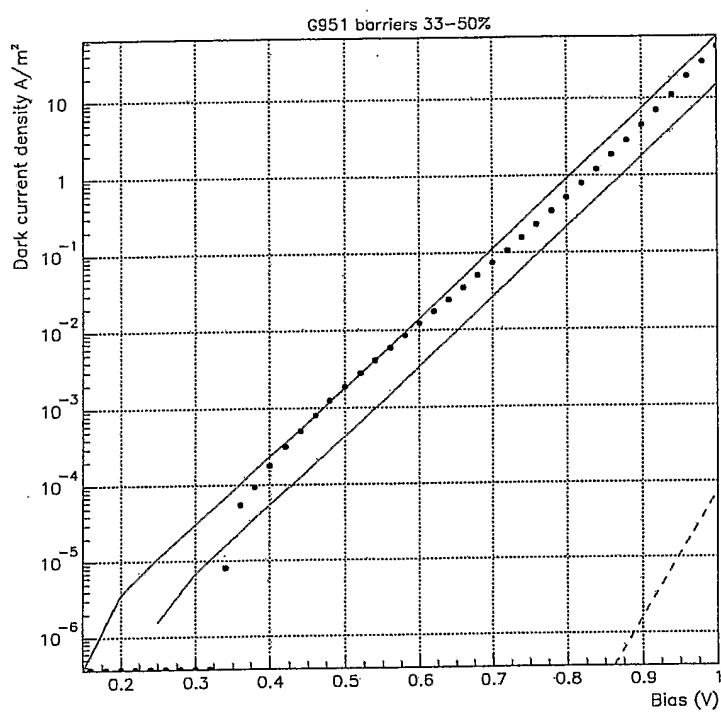


FIGURE 6

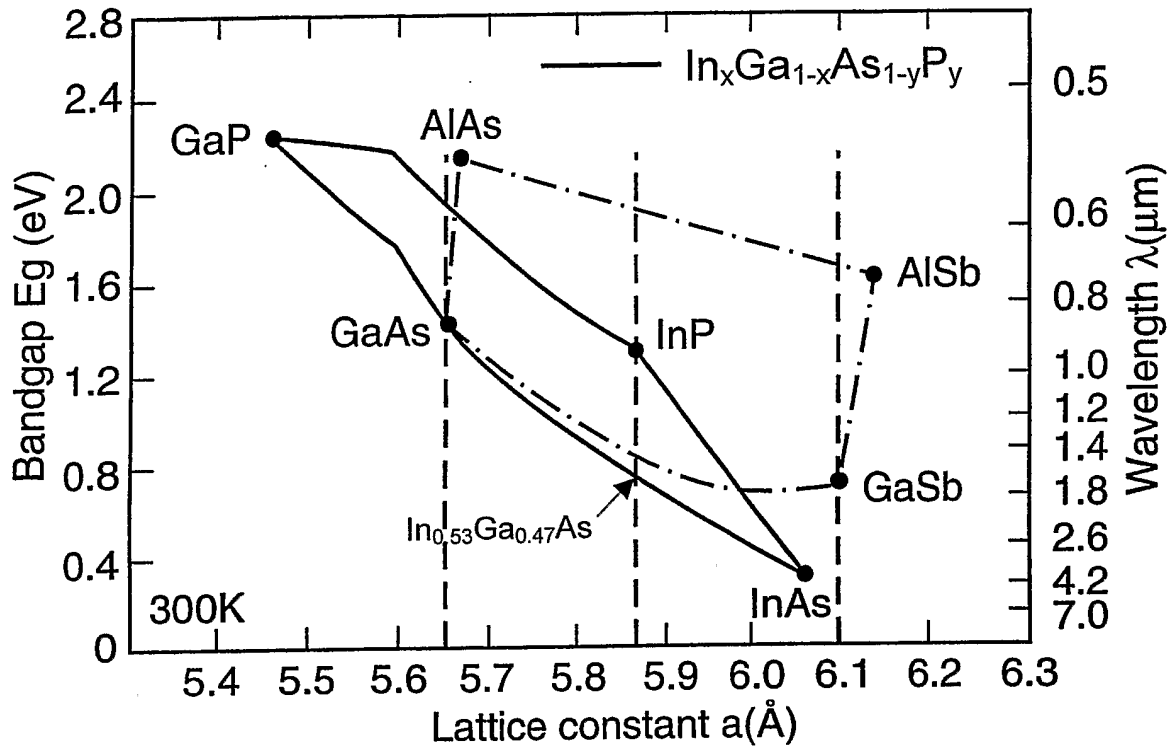


FIGURE 7

INTERNATIONAL SEARCH REPORT

| | |
|----------|-----------------|
| Internal | Application No |
| | PCT/GB 02/03378 |

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01L31/072 H01L31/04 H01L31/075 H01L31/0352

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-----------------------|
| X | US 6 229 152 B1 (FORREST STEPHEN R ET AL) 8 May 2001 (2001-05-08) the whole document | 1-9 |
| A | US 6 150 604 A (IGNATIEV ALEX ET AL) 21 November 2000 (2000-11-21) cited in the application abstract; claims 4,5 | 1-9 |

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents:

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O document referring to an oral disclosure, use, exhibition or other means

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X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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Date of the actual completion of the international search

11 October 2002

Date of mailing of the international search report

21/10/2002

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Werner, A

INTERNATIONAL SEARCH REPORT

Intern application No
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| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT | | |
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| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
| A | <p> GRIFFIN P ET AL: "The application of quantum well solar cells to thermophotovoltaics" SOLAR ENERGY MATERIALS AND SOLAR CELLS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 50, no. 1-4, 1998, pages 213-219, XP004102512 ISSN: 0927-0248 abstract --- </p> | 1-9 |
| A | <p> EKINS-DAUKES N J ET AL: "Strained and strain-balanced quantum well devices for high-efficiency tandem solar cells" SOLAR ENERGY MATERIALS AND SOLAR CELLS, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 68, no. 1, April 2001 (2001-04), pages 71-87, XP004226968 ISSN: 0927-0248 figure 10 --- </p> | 7 |
| A | <p> BARNHAM K ET AL: "VOLTAGE ENHANCEMENT IN QUANTUM WELL SOLAR CELLS" JOURNAL OF APPLIED PHYSICS, AMERICAN INSTITUTE OF PHYSICS, NEW YORK, US, vol. 80, no. 2, 15 July 1996 (1996-07-15), pages 1201-1206, XP000631792 ISSN: 0021-8979 figure 1; table 1 ----- </p> | |

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Information on patent family members

International Application No
PCT/GB 02/03378

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
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| US 6150604 | A | 21-11-2000 | US 5851310 A 22-12-1998 US 6147296 A 14-11-2000 US 6372980 B1 16-04-2002 |