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(54) **Title:** PHOTOVOLTAIC DEVICE

AlGaAs / AlInGaP Cell	~2.0eV	55
InGaP Cell	~1.8eV	54
GaAs Cell	~1.4eV	53
GaNAsBi / InGaNAsBi Cell	~1eV	52
SiGe / SiGeSn Cell	~0.7eV	51
GaAs Substrate	p- or n-type	50

Fig. 6

(57) **Abstract:** A multijunction tandem photovoltaic device is disclosed having a bottom subcell of silicon germanium or silicon germanium tin material and above that a subcell of gallium nitride arsenide bismide, or indium gallium nitride arsenide bismide, material. The materials are lattice matched to gallium arsenide, which preferably forms the substrate. Preferably, further lattice matched subcells of gallium arsenide, indium gallium phosphide and aluminium gallium arsenide or aluminium indium gallium phosphide are provided.



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PHOTOVOLTAIC DEVICE

The present invention relates to photovoltaic devices having more than one subcell for absorbing different parts of the spectrum of the incident light.

Background

Multijunction photovoltaic devices comprise a series of subcells each having a light absorbing semiconductor material and a p-n junction therein to separate the photocarriers, to produce the photocurrent. They work by having a top subcell, i.e. that first exposed to the incident light, that has a large bandgap and so absorbs the shorter wavelengths in the incident light only and passes the longer wavelengths, with the next subcell having a smaller bandgap so that it can absorb part of the light passed by the subcell above, and so on. Solar cells are, of course, one kind of photovoltaic device and are ones used to convert sunlight into electricity for the purpose of generating power.

In this document "top" and "bottom" are to be understood in that sense, i.e. the top subcell is that which receives the incident light first in normal use, rather than the actual spatial orientation of the device. "Above" and "below" are also to be understood similarly, unless the context demands otherwise. Further light is not to be understood as visible light only. For example 1.0 eV and 0.7 eV bandgaps discussed in this document absorb light in the infra-red region.

Multijunction photovoltaic devices often use lattice matched material, which is to say that when one material is grown on another the lattice parameters of the two materials match to

an extent that the crystal structure of the material being grown is maintained and strain relieving dislocations are not introduced. When the lattice parameters of the two materials, in the bulk form, are not quite equal the layer being grown becomes strained, i.e. its lattice parameter changes to match that of the layer on which it grown. Where the strain is quite small the layer being grown can be grown to an arbitrary thickness without the introduction of dislocations. The thickness at which strain relieving dislocations first appear is defined as the critical thickness for a material. In this context, the term lattice matched would also refer to strained layers grown to thicknesses below the critical thickness. Some examples of known multijunction solar cells are as follows.

US2009/00140161 (Harris) describes a triple junction solar cell as shown in Figure 1 of the present application. The structure is an InGaP top subcell, a GaAs middle subcell and a GaInNAsSb bottom subcell, all lattice matched to a GaAs substrate. The aim stated by this document is to improve on the efficiency of a record holding InGaP/InGaAs/Ge solar subcell. For the GaInNAsSb material, it discloses, a bandgap of 0.9 to 1.3 eV and that it can be lattice matched to GaAs, which has a bandgap of 1.42 eV, so a GaInNAsSb subcell can be used to absorb the longer wavelengths passed by the GaAs subcell above it. The proposed proportions of In, N and Sb are respectively 0.05 to 0.07, 0.01 to 0.02 and 0.02 to 0.06. The document discloses experimental results comparing GaInNAsSb junctions to GaInNAs ones with the former achieving a better internal quantum efficiency and so it claims "The GaInNAsSb material system on substrate [GaAs] (FIG. 1A) represents one of the smallest bandgaps ever achieved (0.92eV) in a dilute nitride solar subcell with high carrier collection efficiency." Further it notes a merit of a 0.92eV bandgap

which is that since there is little energy in the solar spectrum between 0.85eV and 0.92eV due to atmospheric absorption, subcells with just smaller bandgaps than that will not provide extra photocurrent. Later it concludes, "Since GaInNAsSb-containing devices produce sufficient current this shows that using this material, rather than Ge, as the bottom junction in a triple-junction GaInP/GaAs/GaInNAsSb device has the potential to increase the power conversion efficiency of triple junction subcells according to the invention by increasing the open-circuit voltage of the devices."

US2011/0232730 (Jones) proposes a lattice matched triple junction solar cell having a similar set of subcells to that of Harris. Figure 2 of the present application shows this structure. Again, the proposed bottom subcell 21 is GaInNAsSb, but the material is described as "low Sb, enhanced In and N". More specifically the proposed proportions of In, N and Sb are respectively 0.07 to 0.18, 0.025 to 0.04 (higher than Harris) and 0.001 to 0.03 (generally lower than Harris). The subcells are lattice matched to the substrate. Possibilities of an Al component in the top subcell 23 and of an In component in the middle subcell 22, marked in Figure 2, are disclosed. These enable the materials to be lattice matched to Ge, when that is the substrate. This document also proposes that when the substrate is Ge there may be a fourth subcell in that substrate.

US2011/0083729 (Lee) also discloses a triple junction solar cell. The structure of Lee is shown in Figure 3 of the present application. Again the top subcell 33 is InGaP, but the middle subcell 32 is GaNAs and the bottom subcell 31 is SiGe. The document notes a problem with Ge bottom subcells, which is that because of the small bandgap the current produced by Ge subcells is high compared to GaAs and InGaP top and middle

subcells leading to inefficiency. The SiGe actually used has a higher bandgap and produces a current that matches that of the InGaP and GaNAs top and middle subcells proposed. In this device the lattice matching is limited. In one example, the top, middle and bottom subcells are lattice matched to each other at 5.641 Å with the subcells having the following compositions $\text{Ga}_{0.544}\text{In}_{0.456}\text{P}$, $\text{Ga}_{0.0092}\text{As}_{0.9908}$, and $\text{Si}_{0.04}\text{Ge}_{0.96}$. However these subcells are not lattice matched to the substrate 30, which may be of various materials, and a metamorphic buffer layer 34 is employed to reduce the strain. This is produced by changing the composition of the buffer layer while it is grown to change the lattice parameter, which is not only a complex operation but will introduce defects into the structure.

GB2467934, also owned by the present applicant company, discloses a multijunction solar subcell, shown in Figure 4 of the present application, which has a InGaP top subcell 43, a GaAs middle subcell 2 and a SiGe subcell 41, all lattice matched to a GaAs substrate 40.

"Theoretical study of the effects of isovalent coalloing of Bi and N in GaAs" by Janotti et al (Physical Review B, Vol. 65, 115203) of 15 February 2002 discloses a theoretical study of $\text{GaAs}_{1-x-y}\text{N}_x\text{Bi}_y$ which concludes that the bandgap of this material when latticed matched to GaAs could be ~1eV.

"Molecular beam epitaxy growth of $\text{GaAs}_{1-x}\text{Bi}_x$ " by Tixier et al (Applied Physics Letter Vol82, No.14 p2245) of 7 April 2003 discloses experimental results for epitaxial layers of $\text{GaAs}_{1-x}\text{Bi}_x$ with the proportion of Bi up to 3% and bandgaps (photoluminescence maximum) down to 1.16eV.

Summary of Invention

According to the present invention there is provided a multijunction photovoltaic device comprising:

a set of semiconductor material layers, the layers including:

a first light absorbing layer of silicon germanium or silicon germanium tin material including a photocarrier separating p-n junction,

a second light absorbing layer of gallium nitride arsenide bismide material, or indium gallium nitride arsenide bismide material, including a photocarrier separating p-n junction,

wherein the silicon germanium or silicon germanium tin layer and the gallium nitride arsenide bismide, or indium gallium nitride arsenide bismide, layer are lattice matched to gallium arsenide.

The multijunction photovoltaic device may further comprise a light absorbing layer of gallium arsenide material including a photocarrier separating p-n junction.

The multijunction photovoltaic device may further comprise a light absorbing layer of indium gallium phosphide including a photocarrier separating p-n junction and being lattice matched to gallium arsenide.

The multijunction photovoltaic device may further comprise a light absorbing layer of aluminium gallium arsenide including a photocarrier separating p-n junction and being lattice matched to gallium arsenide.

The multijunction photovoltaic device may further comprise a light absorbing layer of aluminium indium gallium phosphide

including a photocarrier separating p-n junction and being lattice matched to gallium arsenide.

These additional layers absorb shorter wavelengths than the silicon germanium, or silicon germanium tin, and gallium nitride arsenide bismide, or indium gallium nitride arsenide bismide, layers.

The multijunction photovoltaic device may comprise a gallium arsenide substrate, the set of layers being on and lattice matched to the substrate. Alternatively the multijunction photovoltaic may comprise a substrate that is lattice matched to gallium arsenide, the set of layers being on and lattice matched to the substrate.

The multijunction photovoltaic device may be a solar cell.

The present invention also provides a method of making a multijunction photovoltaic device comprising:

- providing a substrate of gallium arsenide or another material that is lattice matched to gallium arsenide,

- growing a first light absorbing layer of silicon germanium or silicon germanium tin material, including a photocarrier separating p-n junction, lattice matched to the substrate,

- growing a second light absorbing layer of gallium nitride arsenide bismide, or indium gallium nitride arsenide bismide, material, including a photocarrier separating p-n junction, lattice matched to the first light absorbing layer.

The method may comprise growing a light absorbing layer of gallium arsenide material, including a photocarrier separating p-n junction.

The method may comprise growing a light absorbing layer of indium gallium phosphide, including a photocarrier separating p-n junction, lattice matched to gallium arsenide.

The method may comprise growing a light absorbing layer of aluminium gallium arsenide, including a photocarrier separating p-n junction, lattice matched to gallium arsenide.

The method may comprise growing a light absorbing layer of aluminium indium gallium phosphide, including a photocarrier separating p-n junction, lattice matched to gallium arsenide.

The method may comprise providing at least one further layer between two neighbouring ones of the said light absorbing layers, the at least one further layer being lattice matched to gallium arsenide.

The method may comprise removing the substrate.

Preferably the light absorbing layers are arranged in order of bandgap. This may often mean that they are grown in order of bandgap but it would be possible to grow only some of the light absorbing layers, remove the substrate and continue growth in the other direction (a substrate usually being provided on the other side).

The light absorbing layers with their p-n junctions of the invention may, as is known in the art, each be comprised in a respective region of a multijunction photovoltaic device conventionally known as a subcell, which may have further layers.

The gallium nitride arsenide bismide, or indium gallium nitride arsenide bismide, subcell and silicon germanium, or

silicon germanium tin, subcell of the invention are able between them to provide good absorption coverage of the spectral wavelengths longer than those absorbed by, for example, a gallium arsenide subcell, offering high absorption efficiency. This is in contrast of the approach of US2009/00140161 (Figure 1) and US2011/0232730 (Figure 2) which have only one such subcell, and in those the subcell is of a different material, namely GaInNAsSb. Further, the former document explicitly states that the goal is to have as small a bandgap as possible for the GaInNAsSb. Also, in US2011/0083729 (Figure 3) there are GaNAs and SiGe layers that absorb in this general area of the spectrum but GaNAs cannot be lattice matched to GaAs which means that in that device a strain relieving buffer layer has to be used between its subcells and the substrate. Further this device has no subcell in the 1.4eV region that would be provided by GaAs, and none could be provided simply because it would not lattice match the GaNAs - further, the InGaP subcell in this device would in order to lattice match GaNAs have a larger bandgap (by changing the proportion of In and Ga) than the InGaP subcell used in the examples of the present invention which is lattice matched to GaAs, leaving a large gap in the absorption spectrum of the device of US2011/0083729.

As noted above, subcells, both in the invention and as is known generally in the art, may comprise additional layers. For example, as is known in the art, tunnel contacts may be inserted between the light absorbing subcells of multijunction photovoltaic devices, and these may be so used in the present invention, to provide good electrical connection between the subcells, and to allow the p-n junction in the neighbouring subcells to have the same polarity so that current may flow through the device. Window layers and back surface field (BSF)

layers, as also known in the art, are preferably also incorporated into the structure of the device of the invention. A window is usually provided at the top of each cell and a back surface field at the bottom of each subcell and these are preferably provided in the invention. However, as noted later the invention does provide an advantage in relation to these.

Brief description of the drawings

Examples of the invention will now be described, with reference to the accompanying drawings of which:

- FIGURE 1 shows the subcells of a first known multijunction solar cell,
- FIGURE 2 shows the subcells of a second known multijunction solar cell,
- FIGURE 3 shows the subcells of a third known multijunction solar cell,
- FIGURE 4 shows the subcells of a fourth known multijunction solar cell,
- FIGURE 5 shows the subcells of a first example of a multijunction photovoltaic device in accordance with the invention,
- FIGURE 6 shows the subcells of a second example of a multijunction photovoltaic device in accordance with the invention,
- FIGURE 7 is a graph showing the bandgap of GaAs and GaNAs of various compositions and the possibilities of bandgap of GaNAsBi/InGaNAsBi when lattice matched to GaAs, and
- Figure 8 is a graph showing the bandgap and lattice parameter of the alloy SiGeSn, showing that it can be lattice matched to GaAs with a bandgap range of 0.66~1.1eV.

Examples

Figure 5 shows the subcells of first example of a multijunction photovoltaic device, in particular a solar cell, in accordance with the invention. This comprises a series of subcells to absorb incident light, formed on a GaAs substrate 50. The light is first incident on the subcell 54, which in this example is furthest from the substrate, with light not absorbed by each subcell passing to the next. In this example there are a top subcell 54 comprising a light absorbing layer of InGaP material, an upper middle subcell 53 comprising a light absorbing layer of GaAs 52 and a lower middle subcell comprising a light absorbing layer of GaNAsBi or InGaNAsBi material and a bottom subcell 51 comprising a light absorbing layer of SiGe material, all of which are lattice matched to a GaAs substrate 50. The light absorbing material layer of each of these subcells contains a p-n junction to separate the photocarriers generated. Preferably the cells are connected in series (tandem cell).

In this example, additional layers, which are tunnel contacts (which are provided between the subcells to provide good electrical contact), windows and back surface fields, are incorporated into the structure. These are between the subcells and above and below the light absorbing layers as appropriate. These additional layers are also lattice matched to the GaAs substrate, but as their use is well known in the art and for simplicity of illustration these layers not shown in Figure 5 (similarly for Figure 6). Because all the layers are lattice matched, including to the substrate, this reduces the cost of manufacture and enhances device performance, reliability and yield. Another advantage of this example is the ability, compared to devices having a Ge substrate with a light absorbing subcell in that, to put a back surface field (BSF) below the p-n junction of SiGe bottom sub-cell for

enhanced device performance. Additionally, a sacrificial release layer that has a differential etch rate to GaAs may be grown below the SiGe subcell. This permits the epitaxial layer structure containing the subcells to be removed from the GaAs substrate and transferred to a suitable handle or heat sink, allowing the GaAs substrate to be re-used and if needed reducing the weight of the device. These additional layers are grown epitaxially on the GaAs substrate before the SiGe subcell is grown. Alternatively the subcells may be grown in reverse order on a GaAs substrate (or a substrate lattice matched to GaAs) starting with the widest bandgap (the InGaP subcell in the case of Figure 5) and then followed by the narrower bandgap subcells in order (the GaAs subcell, then the GaNAsBi / InGaNAsBi subcell and then the SiGe / SiGeSn subcell in the case of Figure 5). A sacrificial layer is provided between the widest bandgap subcell and the GaAs substrate allowing the subcells to be removed and transferred to a suitable handle or heat sink, inverted so that the narrowest bandgap cell is next to the handle or heart sink and the widest bandgap cell receives the incident light first.

The composition of the light absorbing GaNAsBi layer of subcell 52 is such that its bandgap is preferably in the range $0.8 < E_g < 1.2\text{eV}$. A bandgap of around 1.0 eV is particularly advantageous since it fills the gap between the parts of the spectrum absorbed by the SiGe and GaAs layers.

Figure 7 is a graph showing the bandgap of various Group III-V semiconductor materials and Group IV materials versus their lattice parameter. There are of course numerous III-V materials but the ones shown are selected either to illustrate the GaNAsBi / InGaNAsBi material used in the light absorbing layer of subcell 52 of the invention or for general comparison with well-known materials. In particular a dot-dashed line 71

extends between the point for GaAs and the point for GaBi (off the graph as it has a negative bandgap) giving the values for the ternary compound $\text{GaAs}_{1-y}\text{Bi}_y$ as the proportion y of Bi atoms varies. Dotted line 72 extending from the point for GaAs towards that for GaN, which is off the graph shown at a smaller lattice parameter, giving the values for the ternary compound $\text{GaAs}_{1-x}\text{N}_x$ as the proportion x of N atoms varies. This Figure shows that the substitution of a proportion the As atoms in GaAs by either N or Bi to GaAs reduces the bandgap (even to the range of that of Ge - while it is not practical to add more than a few percent of N that is sufficient to reach the bandgap of Ge). However substituting in N reduces the lattice parameter, while substituting in Bi increases the lattice parameter. It turns out that substituting in both N and Bi for As, i.e. to form the quaternary material $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$, still causes the bandgap to decrease from that of GaAs and with certain proportions of N and Bi the material is lattice matched to GaAs (the effects on lattice parameter of N and Bi cancelling each other out). An exact lattice match to GaAs is shown by the vertical dashed line, but strained materials having layer thicknesses below the critical thickness are also possible and lie to either side of the dashed line. The shaded area shows possibilities for the quaternary GaNAsBi having bandgaps of the most interest in the invention. Note, in particular, that the region neighbouring the dashed vertical line (which is the lattice matched region) that is within the shaded area also does include bandgaps in the region of 1eV between that of SiGe (around 0.7eV) and GaAs (around 1.4eV).

Figure 7 also shows a solid line 73 for the ternary material $\text{In}_z\text{Ga}_{1-z}\text{As}$. This shows that the effect of In is to reduce the bandgap from GaAs while increasing the lattice parameter. In those respects its effect is similar to that of Bi, so both Bi

and In can be used to balance the lattice parameter against the effect of N to provide a lattice match to GaAs, while all three (Bi, In and N) reduce the bandgap from that of GaAs. So the material $\text{In}_z\text{Ga}_{1-z}\text{N}_x\text{As}_{1-x-y}\text{Bi}_y$ used in some of the examples of the invention given above also provides a lattice match to GaAs for a range of bandgaps between those of GaAs and SiGe / SiGeSn.

The precise proportions of N and Bi in the GaNAsBi for a particular bandgap and lattice matching can of course be experimentally determined easily for any particular case. However for lattice matching to GaAs the ratio of N to Bi is about 1:1.7. For bandgaps equal to GaAs (1.4eV) down to 0.9eV the respective proportion of N and Bi, x and y, in the material lie in the range $0 < x < 6\%$ and $0 < y < 11\%$.

For the material $\text{In}_z\text{Ga}_{1-z}\text{N}_x\text{As}_{1-x-y}\text{Bi}_y$ used in some of the examples above the range for the proportion of In, z, is $0 < z < 15\%$, with the ranges for the proportions of N and Bi being as noted above for $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$.

To make the SiGe light absorbing layer in subcell 51 lattice matched to GaAs the proportion of silicon is around 0.018 and this material then has a bandgap of around 0.7eV. As can be seen in Figure 8, which is another graph showing the bandgap of various Group III-V semiconductor materials and Group IV materials versus their lattice parameter, Ge is not lattice matched to GaAs but as the difference is not large only a small amount of Si needs to be added to achieve the lattice matching. Since SiGe is a binary compound there is only one degree of freedom provided by the proportion of the atoms and so the bandgap is fixed at around 0.7eV if the lattice match to GaAs is to be maintained.

However, if desired a larger bandgap can be obtained for subcell 51 by using SiGeSn instead of SiGe. This material is lattice matched to GaAs where the ratio of Si to Sn is approximately 4:1. Where for example the proportion of Si is 2% and that of Sn is 0.5% this provides a larger bandgap than SiGe lattice matched to GaAs, where the proportion of Si is 8% and that of Sn is 2% the bandgap is wider, and where the proportions are much larger the bandgap can extend further.

Figure 6 shows the subcells of a second example of the invention. This device is as that of Figure 5 but it has an additional subcell 55 having a light absorbing layer and a photocarrier separating p-n junction located above the InGaP subcell 54. This subcell 55 absorbs part of the spectrum above around 2.0 eV and allows longer wavelengths to be absorbed by the InGaP subcell 54 and the subcells below that. The material of the light absorbing layer of this subcell 55 in this example is AlGaAs having a proportion of Al and Ga having the desired bandgap. This material is lattice matched to GaAs, although strained, at all proportions of Al to Ga, and can be grown to thicknesses required for a photovoltaic device to have sufficient absorption without any strain relaxation.

In another similar example the light absorbing material layer of subcell 55 is AlInGaP lattice matched to GaAs. Again the bandgap of is preferably about 2.0eV but since the material is a quaternary some extra flexibility is obtained.

The subcells examples of Figures 5 and 6 described above do not, as is preferred, have further subcells between them. That is however possible with preferably the bandgaps of the light absorbing materials of the intervening subcells being between that of their neighbours.

Note also that while the substrate of the examples is GaAs the invention also extends to cases where the substrate on which the subcells are grown is another material that is lattice matched to GaAs.

Note further that if not needed for certain applications any one or more of subcells 53, 54 or 55 can be omitted.

The materials of the subcells may be grown using epitaxial techniques including MBE and MOCVD.

For example, GB2467934, also owned by the present applicant company and mentioned above, discloses examples of SiGe materials manufactured on GaAs substrates. The document is incorporated herein by reference. These materials can be grown using an epitaxy process, using a germanium containing precursor (e.g. GeH_4 , GeCl_4 , etc.) and a silicon containing precursor (e.g. SiH_4 , SiH_2Cl_2 , SiHCl_3 , disilane etc.) with a carrier gas (e.g. H_2). The p-n junction used to separate the photo carriers may be formed in the SiGe material by various methods. These include doping during the epitaxial growth, or by diffusion in of dopant into a layer of the material when it is grown or is partially grown. An alternative method is given below.

The SiGe or SiGeSn material used in subcell 51 will in many examples have III-V material directly grown on it. There may then be diffusion of Group V atoms from the III-V material into the SiGe or SiGeSn. Arsenic atoms, for example, will do this. Arsenic in SiGe or SiGeSn is an n-type dopant.

So if the SiGe or SiGeSn neighbouring the III-V material grown on it is p-type then the Group V atoms diffusing into the SiGe or SiGeSn may well dope the SiGe or SiGeSn forming a p-n junction below the surface of the SiGe or SiGeSn. (If this

junction were to be parasitic in a particular example it can be prevented or controlled by forming a thin Si diffusion barrier between the SiGe or SiGeSn. Three atomic layers is sufficient.) However, as foreshadowed, the junction so formed can be utilised as the photocarrier separating junction in the SiGe or SiGeSn subcell. Alternatively it may be used as a tunnel diode between the SiGe or SiGeSn subcell and the subcell grown on that. A thinner Si barrier can be used to control the amount of diffusion if that is desired.

On the other hand if the SiGe or SiGeSn neighbouring III-V material grown on it is n-type (i.e. an epitaxially grown SiGe or SiGeSn p-n junction) the diffusion in of Group V atoms will not form an extra p-n junction.

The GaNAsBi / InGaNAsBi layer of the invention is also formed by epitaxy. The p-n junction for separating the photocarriers therein is formed either by doping during the epitaxial growth, or, alternatively, after the layer, or part thereof has been grown and diffusing the dopant in. This material could be grown by any epitaxial process such as MBE, MOCVD etc.

GB2467934, and also GB2467935 also owned by the present applicant, describe techniques that may be employed in the present invention to remove the GaAs substrate from the rest of the device. Those documents are therefore incorporated by reference. This is useful, for example, to reduce weight of the device (useful for space applications), to allow a heat sink to be bonded to the device or to allow the substrate to be re-used to reduce cost.

The GaAs substrate may be removed when all the subcells have been grown in order on it (which may be in either order). Alternatively the GaAs substrate can be removed at any point during the growth and that may be part way through a subcell

including partway through the just one cell. In these methods a new substrate is mounted on the just grown surface.

CLAIMS:

1. A multijunction photovoltaic device comprising:
a set of semiconductor material layers, the layers including:
a first light absorbing layer of silicon germanium or silicon germanium tin material including a photocarrier separating p-n junction,
a second light absorbing layer of gallium nitride arsenide bismide material, or indium gallium nitride arsenide bismide material, including a photocarrier separating p-n junction,
wherein the silicon germanium or silicon germanium tin layer and the gallium nitride arsenide bismide, or indium gallium nitride arsenide bismide, layer are lattice matched to gallium arsenide.
2. A multijunction photovoltaic device as claimed in a claim 1 wherein the second light absorbing layer is of gallium nitride arsenide bismide material.
3. A multijunction photovoltaic device as claimed in a claim 1 wherein the second light absorbing layer is of indium gallium nitride arsenide bismide material.
4. A multijunction photovoltaic device as claimed in any one of claims 1 to 3 further comprising a light absorbing layer of gallium arsenide material including a photocarrier separating p-n junction.
5. A multijunction photovoltaic device as claimed in any preceding claim further comprising a light absorbing layer of indium gallium phosphide including a photocarrier separating p-n junction and being lattice matched to gallium arsenide.

6. A multijunction photovoltaic device as claimed in any preceding claim further comprising a light absorbing layer of aluminium gallium arsenide including a photocarrier separating p-n junction and being lattice matched to gallium arsenide.

7. A multijunction photovoltaic device as claimed in any one of claims 1 to 5 further comprising a light absorbing layer of aluminium indium gallium phosphide including a photocarrier separating p-n junction and being lattice matched to gallium arsenide.

8. A multijunction photovoltaic device as claimed in any preceding claim comprising a gallium arsenide substrate, the set of layers being on and lattice matched to the substrate.

9. A multijunction photovoltaic device as claimed in any one of claims 1 to 7 comprising a substrate that is lattice matched to gallium arsenide, the set of layers being on and lattice matched to the substrate.

10. A multijunction photovoltaic device as claimed in any preceding claim wherein the photovoltaic device is a solar cell.

11. A method of making a multijunction photovoltaic device comprising:

providing a substrate of gallium arsenide or another material that is lattice matched to gallium arsenide,
growing a first light absorbing layer of silicon germanium or silicon germanium tin material, including a photocarrier separating p-n junction, lattice matched to the substrate,

growing a second light absorbing layer of gallium nitride arsenide bismide, or indium gallium nitride arsenide bismide, material, including a photocarrier separating p-n junction, lattice matched to the first light absorbing layer.

12. A method as claimed in claim 11 wherein the second layer is of gallium nitride arsenide bismide material.

13. A method as claimed in claim 11 wherein the second layer is of indium gallium nitride arsenide bismide material.

14. A method as claimed in any one of claims 11 to 13 comprising growing a light absorbing layer of gallium arsenide material, including a photocarrier separating p-n junction.

15. A method as claimed in any one of claims 11 to 14 comprising growing a light absorbing layer of indium gallium phosphide, including a photocarrier separating p-n junction, lattice matched to gallium arsenide.

16. A method as claimed in any one of claims 11 to 15 comprising growing a light absorbing layer of aluminium gallium arsenide, including a photocarrier separating p-n junction, lattice matched to gallium arsenide.

17. A method as claimed in in any one of claims 11 to 15 comprising growing a light absorbing layer of aluminium indium gallium phosphide, including a photocarrier separating p-n junction, lattice matched to gallium arsenide.

18. A method as claimed in any of claims 11 to 17 comprising providing at least one further layer between two neighbouring ones of the said light absorbing layers, the at least one further layer being lattice matched to gallium arsenide.

19. A method as claimed in any of claims 11 to 18 comprising removing the substrate.

InGaP Cell	13
GaAs Cell	12
GaInNAsSb Cell	11
GaAs Substrate	10

Fig. 1

(Al)InGaP Cell	23
(In)GaAs Cell	22
Low Sb, enhanced In and N GaInNAsSb Cell	21
Substrate (possibly including Ge Cell)	20

Fig.2

InGaP Cell	33
GaNAs Cell	32
SiGe Cell	31
Buffer	34
Substrate	30

Fig. 3

InGaP Cell	43
GaAs Cell	42
SiGe Cell	41
GaAs Substrate	40

Fig. 4

InGaP Cell	~1.8eV	54
GaAs Cell	~1.4eV	53
GaNAsBi / InGaNAsBi Cell	~1eV	52
SiGe / SiGeSn Cell	~0.7eV	51
GaAs Substrate	p- or n-type	50

Fig. 5

AlGaAs / AlInGaP Cell	~2.0eV	55
InGaP Cell	~1.8eV	54
GaAs Cell	~1.4eV	53
GaNAsBi / InGaNAsBi Cell	~1eV	52
SiGe / SiGeSn Cell	~0.7eV	51
GaAs Substrate	p- or n- type	50

Fig. 6

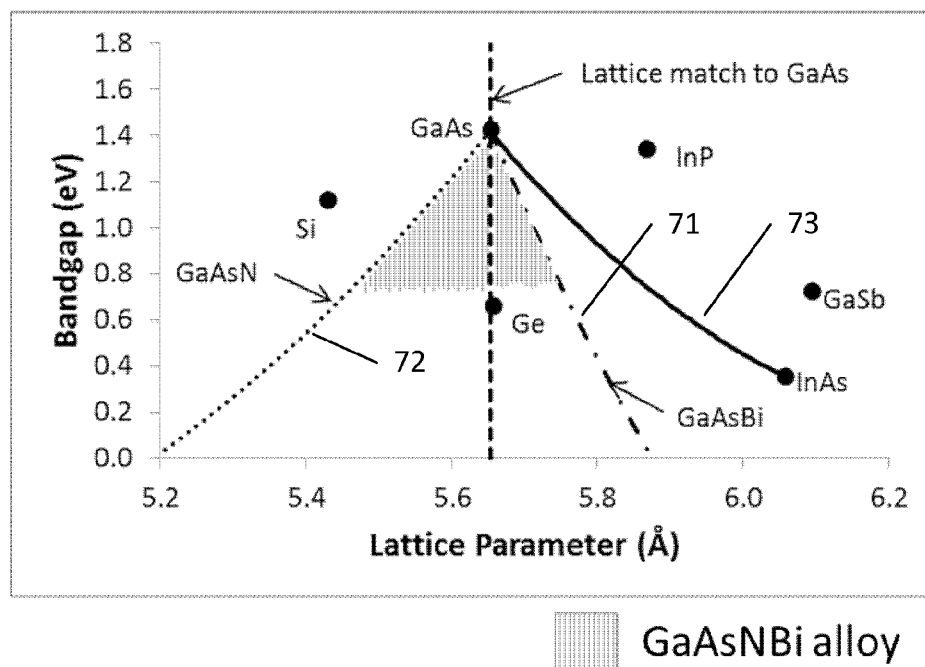


Fig. 7

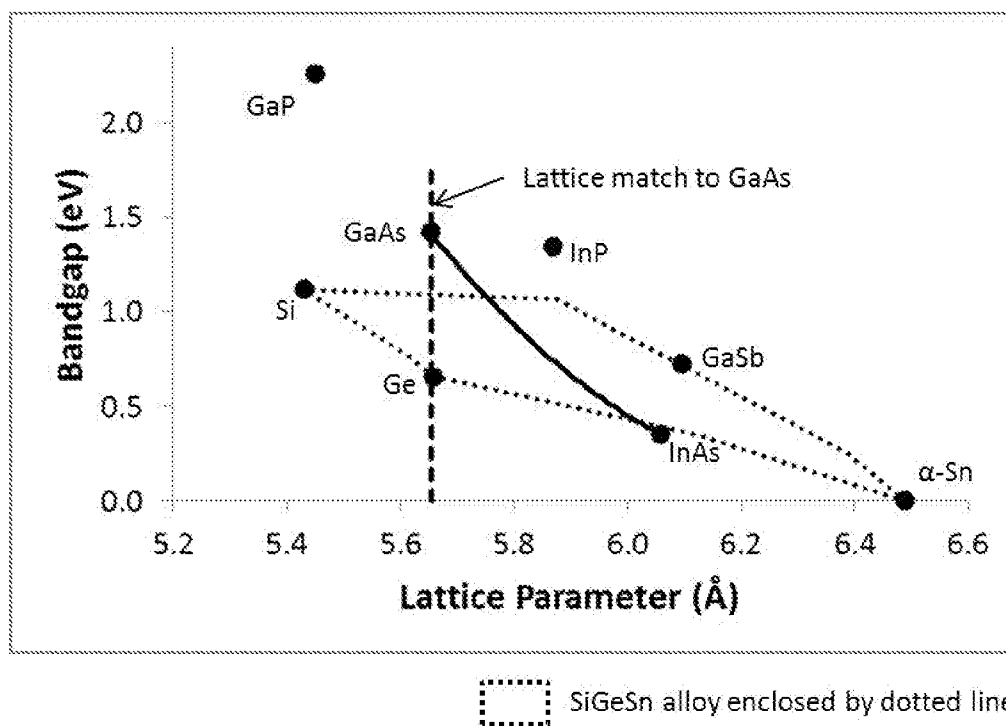


Fig. 8

INTERNATIONAL SEARCH REPORT

International application No

PCT/GB2012/051980

A. CLASSIFICATION OF SUBJECT MATTER

INV. H01L31/0328 H01L31/0687 H01L31/0725
ADD.

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)

H01L H01G

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 practicable, search terms used)

EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2010/102345 A1 (CUNNINGHAM SHAUN JOSEPH [AU]) 16 September 2010 (2010-09-16) page 2, line 20 - page 3, line 3 page 5, lines 15-31 page 6, lines 23-25 page 36, line 6 - page 38, line 10; figure 2	1-19
Y	GB 2 467 934 A (IQE SILICON COMPOUNDS LTD [GB]) 25 August 2010 (2010-08-25) cited in the application page 1, line 20 - page 2, line 15 page 3, line 1 - page 6, line 14 page 8, line 9 - page 11, line 9; figures 1-3 ----- -/--	1-19



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

27 November 2012

Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2012/051980

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

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International application No

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