An indium phosphide photovoltaic cell is provided where one or more quantum wells are introduced between the conventional p-conductivity and n-conductivity indium phosphide layer. The approach allows the cell to convert the light over a wider range of wavelengths than a conventional single junction cell and particularly convert efficiently transparency losses of the indium phosphide conventional cell. The approach hence may be used to increase the cell current output.

A method of fabrication of photovoltaic devices is provided where ternary InAsP and InGaAs alloys are used as well material in the quantum well region and results in an increase of the cell current output.

12 Claims, 3 Drawing Sheets
**FIG. 3**

PL10 K

InP/InAs(x)P(1−x) MULTI-QUANTUM WELLS

CALCULATED

X=0.6 ——

X=0.5 ——

EXPERIMENTAL

X=0.55 △

X=0.5 □

X=0.6 ○

**FIG. 4**

InP/InAsP MQWs(p/i/n) —— InP(p/n) ——

NORMALIZED SPECTRAL RESPONSE

WAVELENGTH (nm)
A "quantum well" is briefly defined as a heterostructure. The insertion of a barrier material provides improved photocurrent output and extends the effective band gap for absorption to longer wavelengths.

Weinberg, D. J. Flood, in Band Gap Absorbing Material, which maximizes light absorption, and a high band gap absorbing material, which maximizes output voltage.

Applied to photovoltaic (PV) applications, InP has been shown to be more radiation-resistant than GaAs or Si and therefore more suitable for space applications (J. Weinberg, D. J. Flood, in Progress in Photovoltaics, John Wiley & Sons Ltd, 1993). Radiation resistance can be an important property of solar cells for space application, since the devices are directly exposed to charged particles from the sun and an extended lifetime is needed for communication satellites and other applications. In theory, higher efficiencies in InP technology are possible with tandem cells, but absorption of longer wavelength light than is absorbed by the InP cell. The improved indium phosphide-based quantum well solar cell should consequently result in an additional increase of the short circuit currents and, when other parameters are optimized, in device efficiency.

SUMMARY OF THE INVENTION

A single-junction Indium Phosphide-based solar cell to achieve higher conversion efficiencies over an extended wavelength of radiation is provided. The insertion of a multi-quantum well (MQW) in the intrinsic region of a (p-i-n) InP solar cell can enhance considerably the efficiency by converting the band gap of indium phosphide to longer wavelengths than is absorbed by indium phosphide. The improved indium phosphide-based quantum well solar cell should consequently result in an additional increase of the short circuit currents and, when other parameters are optimized, in device efficiency.

An Indium Phosphide (InP) based solar cell having a quantum well region sandwiched between the conventional n-type and p-type regions of the cell is provided. It is shown that such quantum well solar cell extends the cell photoconversion to wider wavelength region than a traditional p-n junction cell. The onset wavelength of absorption or photocconversion is provided by the indium phosphide. It is also demonstrated that compared to a traditional p-n junction cell the quantum well solar cell exhibits a much more efficient conversion of photons located in the vicinity of the band gap of the material used for the traditional p- and n-layers. Therefore, a quantum well solar cell can perform efficiently with...
thinner base thickness than those usually required for the traditional counterpart cells. Although experimental demonstrations have been made using a base thickness of 1 micrometer, it is believed, based on theoretical predictions, that even with base thickness in the range of 0.5 microns the relative degradation of the photocurrent characteristics is expected to be less than 5% for the QW cell while the degradation of the short circuit current characteristics and efficiency for the traditional cell exceeds 30%. The MQW cell can then be utilized to achieve higher radiation resistance and/or efficient heteroepitaxial cells. In general, defects generated in the cell result in a reduction of minority carrier diffusion lengths and hence a reduction in cell efficiency.

In one embodiment, the quantum well region is fabricated using indium gallium arsenide and indium phosphide acting respectively as well and barrier materials in the solar cell. In a second embodiment strained InAsP is provided as well material. In a third embodiment tensile strained InGaP barriers are utilized in combination with InAsP wells to enhance the mechanical stability of the cells and prevent a degradation of device characteristics with increasing number of wells.

A method of growing the MQW solar cells is provided, the growth temperature being between about 300°C and about 650°C.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a sketch of a solar cell having multiple quantum wells.

FIG. 2 is a graph comparing the spectral response of an indium phosphide quantum well solar cell (20 periods of InGaAs (6 nm) and InP(20 nm)) and a state-of-the-art indium phosphide solar cell.

FIG. 3 is a graph showing the variation of the apparent band gap of different alloys of InAsP/InP quantum wells as a function of the well thickness.

FIG. 4 is a graph comparing spectral response of an indium phosphide quantum well solar cell (10 periods of InAsP (6 nm) and InP(20 nm)) and a state-of-the-art indium phosphide solar cell.

FIG. 5 shows high-resolution X-ray diffraction patterns of 5, 10, and 30 period strained InAsP/InP quantum well solar cells.

FIG. 6 shows high-resolution X-ray diffraction pattern of a 30 period quantum well solar cell where the barrier material is InGaP (Ga composition of about 15%).

DETAILED DESCRIPTION OF PREFERRED EMBODIMENT

Referring to FIG. 1, an MQW system incorporated into the intrinsic region of a conventional p-i-n indium phosphide (InP) solar cell is shown. The cell is fabricated on substrate 12, the top layer of which is lattice-matched to indium phosphide and the bottom surface of which has thereon back contact 10. Indium phosphide or other suitable materials well-known in the art may be used as a substrate with buffer layers to accommodate crystal lattice-matching requirements between the substrate and the top layer of the substrate. A cell of indium phosphide, consisting of back surface field 14, base 16, intrinsic region 18, and emitter 20, is shown. Other alloys may be used if lattice-matched with indium phosphide. The cell is grown by any known technique, such as liquid phase epitaxy (LPE), metal-organic chemical vapor deposition (MOCVD), or chemical beam epitaxy (CBE). CBE is a low-pressure (pressure less than 0.01 torr) growth technique using all gas or a combination of gas and solid source precursors. The gases can be either organometallics or hydrides of the elements of the desired alloys and dopants. Solid sources can be metals or metalloids of the desired alloys and dopants.

In the solar cell of this invention, intrinsic region 18 includes one or more quantum wells 19. The general requirements for achieving a satisfactory solar cell device, regardless of the nature of the quantum well materials, are that the quantum wells should be fabricated within the space charge region of the conventional p-n junction. This requires that the dopant levels in the intrinsic region of the cell be below about 5x10^16 cm^-3. A more preferred upper limit for the background dopants level in the QW region is 1x10^16 and the most preferred condition is to have a background doping level below 5x10^15 cm^-3.

The lowest possible background doping level is usually a function of the purity of the source materials and growth chamber conditions, as known to those skilled in the art of growing semiconductor films.

Because different elements are used in the fabrication of the heterostructures of this invention, in particular arsenic and phosphorus, it is necessary to grow the films with systems that provide fast switching between the flux and growth precursor elements and fast flux stabilization. Preferably, the switching and stabilization are attained in less than 10 seconds and more preferably in less than 1 second.

The fabrication systems should also allow for a reasonably good control of the growth temperature and temperature fluctuations across the substrate should not exceed 50°C and more preferably should not exceed 10°C. The system should also provide a reasonable uniformity in the flux distribution across the substrate. During the fabrication of a given layer, relative changes in composition or thickness should not exceed 30% and more preferably should not exceed 5%.

The process temperatures for all the steps subsequents to the fabrication of the quantum well region should be maintained as low as practical to prevent degradation of the characteristics of the cell. Preferably, growth temperatures are kept below 650°C, more preferable is growth temperature below 600°C and most preferred is temperatures below 530°C.

The growth conditions outlined above can be achieved in commercially available, MBE, CBE, or MOVPE systems, or in any type of hybrid combination of these growth systems or other standard III-V semiconductor fabrication techniques. The solar cells and quantum wells described herein have been fabricated using CBE. The apparatus and procedures suitable for use in the method of this invention are described in U.S. Pat. No. 5,407,491, which is hereby incorporated by reference for all purposes. Specifically, a Riber CBE32 system was utilized to grow the films described herein. Epitaxial growth occurs in a chamber from precursor material provided from solid source containers, from a high temperature channel through which hydride or other gases may enter the chamber and from a low-temperature channel through which organo-metallic compounds enter the chamber. A pyrometer is placed so as to measure the temperature of the surface of the epitaxial growth. A scanning electron gun and fluorescent screen are used to monitor crystal lattice-matching. Gases are provided to the chamber from sources through mass flow controllers and valves. Organometallic compounds containing precurs-
sor elements are added in bubblers and carried to the chamber in hydrogen gas.

Referring again to FIG. 1, quantum wells are grown in intrinsic region 18 at temperatures most preferably below about 530° C. Metal-organic compounds such as trimethylindium (TMI), triethylindium (TEI), and triethylgallium (TEG) are used to provide indium and gallium at the required temperatures. Pre-cracked arsine (AsH₃) is also employed in the proper proportions as a growth precursor.

The number of wells and barriers that can be included in a solar cell is a function of the background impurity concentration (N) and dielectric constant (ɛ) of the material in the intrinsic region. The total thickness of the quantum well region in the solar cell of this invention should be below the associated space charge width (W) given by

\[ W = \left( \frac{2eV_{bi}}{qN} \right)^{1/2} \]

V is the built-in voltage of the one-side abrupt junction potential (about 0.9 volt for indium phosphide) and q is the electron charge. For a background impurity level of 1x10¹⁵ cm⁻³, W exceeds 1 micron. Given a thickness d₁ for the well region and a thickness d₂ to the barrier region, the number of periods that can be realized is an integer n that is smaller than W/d₁+d₂.

The materials used in the solar cells of this invention are limited to indium phosphide and alloys in the indium phosphide system. The following alloys are here considered alloys in the indium phosphide system: AlInAs, GaAsSb, InAsSb, AlPbSb, GaPbSb, GaInAs, GaInAsSb, AlInSb, GalnPbSb, AlInSb, GaInPbSb, AlInPb, AlGaPbSb. These alloys have somewhat different energy band gaps, which may be desirable in some applications, and may be used as sub-cells. Similarly, indium gallium arsenide is used herein to include all alloys of indium gallium arsenide with the addition of iso-valent elements such as phosphorous, aluminum, and antimony in concentrations such that the lattice mismatch is less than 0.3 per cent compared to In₀.₅Ga₀.₄₅As.

Lattice-matching can be defined as no more than a 0.3 per cent variation in the lattice parameter with respect to the indium phosphide lattice constant; the lattice constant of the material in the indium phosphide system should be established prior to the fabrication of the device of this patent. Relative fluxes and growth temperatures and growth rates (usually growth system dependent) necessary to achieve lattice matching conditions and low impurity backgrounds need to be established prior to undertaking device fabrication. The alloy composition can be checked by X-ray diffraction of any other standard technique used for this purpose.

The method of fabrication is now provided for an InₓGa₁₋ₓAs (0.48≤x≤0.55) and indium phosphide quantum well solar cell.

The quantum well region is fabricated by growing one or more periods of quantum wells. First, a barrier layer consisting of non-doped InP is deposited on the solar cell base. There is no upper limitation on this layer thickness. However, preferably this layer thickness is kept below 100 nm and most preferably below 50 nm. Then the growth of InGaAs is initiated to form a quantum well. The thickness of the well material is preferably between 0.3 and 20 nm, more preferably between 1 nm and 10 nm, and most preferably between 3 nm and 9 nm. The thickness of the well sets the onset for the absorption in the quantum well to the desired value. The InGaAs layer is then capped with an InP layer. The thickness of the top barrier is again kept below 100 nm.

A multiple quantum well (MQW) can be inserted by repeating the growth of InGaAs and InP layers. In order to achieve high quality quantum wells it is preferable to keep the growth temperature constant during the growth of the entire quantum well region. Furthermore, during the switching from InP to InGaAs the growth can be interrupted under phosphorous flux by stopping the In precursor. However, it is preferred to avoid long exposures of the InP surface to arsenic. Prior to the growth of InGaAs, phosphorous flux needs to be interrupted and As, In, and Gallium flux switched on. The interruption time once the phosphorus has been switched off and before turning on other elements should not exceed 10 sec. Furthermore, the surface should not be exposed for periods exceeding 30 seconds to As flux.

The desired pressure range in the chamber depends on precursor compounds used and other factors, but is preferably in the range from about 10⁻⁷ torr to about 10⁻⁵ torr. More preferably, the pressure in the chamber should be between 10⁻⁸ and 5x10⁻⁹ torr. The pressure measured in the chamber must be representative of the pressure at the substrate location.

After the quantum well region is achieved, the top emitter 20 is epitaxially grown. This emitter is preferably grown at a temperature below 650° C. and more preferably at a temperature below 550° C. and most preferably at a temperature below 530° C., so as to leave intact the properties of the multi-quantum well region. The lower range of temperature may be as low as 300° C. Contact layer 22 and front contact 24 are then applied using well-known methods.

An antireflection coating 26 is usually applied over the top of the device. Although indium phosphide is shown in FIG. 1, it should be clear that alloys in the indium phosphide system that are lattice-matched to indium phosphide may be also used.

FIG. 2 shows the spectral response of an InP quantum well solar cell fabricated using 20 periods of InGaAs (6 nm thick) and InP (20 nm thick) (solid line) and the spectral response of a state-of-the-art InP cell (dashed line). It is clear from the spectral response curves that the quantum well region extends the effective band gap for photon conversion to far below the energy band gap of InP. An appreciable photoresponse for the MQW cell is found for wavelengths in the 900 to 1500 nm region. This shows the effectiveness of the quantum wells in increasing the photoresponse of solar cells.

Strained alloys or binary materials in the indium phosphide system can also be used to form quantum wells. Strain in the quantum wells adds an additional degree of freedom toward the tailoring of band gap properties. However, one of the major shortcomings associated with the use of strained materials is related to the fact that special attention should be given to maintain the thickness of individual layers below a critical value, often referred to as the critical thickness where defect generation processes are initiated. Greater thicknesses lead to a degradation of the materials is optical and electric properties. Furthermore, in an association of several quan-
Quantum well solar cells of indium phosphide were grown using the method of this invention. A back surface field having a thickness of about 1 micron was grown. Silicon dopant concentration was at least about 2x10^{18} cm^{-3}. Growth temperatures were in the range from about 480° to 550° C. A base layer having thickness in the range from about 1 to 5 microns was then grown. Silicon dopant concentrations were in the range of 0.4 to 5x10^{17} cm^{-3}. Growth temperatures were in the range from 490° to 550° C. A quantum well region was then fabricated. The total thickness of this region was between 0.1 and 0.8 microns. No dopant was used and growth temperatures were between 460° and 530° C. An emitter layer having thickness in the range from 0.1 to 0.6 microns was then grown. Beryllium concentration were greater than 10^{16} per cm^{-3}. Growth temperatures were in the range of 460° to 530° C. A metallization layer was then added using standard techniques.

All solar cells were fabricated using identical n- and p-doping levels and the (p-emitter) and (MQW-n base) thickness was kept constant in all the samples. Table 1 shows structural parameters of the cells. Doping and thickness parameters were previously optimized for conventional indium phosphide (p/n) solar cells (conventional cell AM 1.5 efficiencies are 13% without antireflection coating (ARC) and 18.7% with ARC) and were reported in U.S. Pat. No. 5,407,491, referenced above). Well and barrier widths were kept constant and equal to 6 nm and 20 nm, respectively. 10, 20, and 30 period quantum wells were included in the intrinsic region of the cell. Gold was utilized as front and back ohmic contacts. Typical cell active area (corrected for grid shadowing) was 0.047 cm².

**TABLE 1**

<table>
<thead>
<tr>
<th>Region</th>
<th>Material</th>
<th>Thickness</th>
<th>Doping Level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact</td>
<td>InGaAs(p)</td>
<td>0.2 μm</td>
<td>3x10^{18}</td>
</tr>
<tr>
<td>Emitter</td>
<td>InP(p)</td>
<td>0.2 μm</td>
<td>2x10^{18}</td>
</tr>
<tr>
<td>Intrinsic or</td>
<td>MQW</td>
<td>3x10^{16}</td>
<td></td>
</tr>
<tr>
<td>(1) MQW of</td>
<td>InGaAs/InP</td>
<td>N × 0.026</td>
<td>&lt;10^{15}</td>
</tr>
<tr>
<td>InGaAs/InP</td>
<td></td>
<td>N = 10,20,30</td>
<td></td>
</tr>
<tr>
<td>(2) MQW of</td>
<td>InGaP/InP</td>
<td>N × 0.026</td>
<td>&lt;10^{15}</td>
</tr>
<tr>
<td>InGaP/InP</td>
<td></td>
<td>N = 5,10,20,30</td>
<td></td>
</tr>
<tr>
<td>InP(n)</td>
<td>2-(N × 0.026) μm</td>
<td>1 × 10^{17}</td>
<td></td>
</tr>
</tbody>
</table>

As expected, the addition of MQWs in the intrinsic region of the indium phosphide solar cells extends the effective band gap for absorption toward longer wavelengths (up to 1500 nm for InGaAs/InP MQWs). Typical spectral response of an indium phosphide (p-MQW-n) solar cell containing InGaAs wells is represented in FIG. 2 and is characterized by a non-negligible photocurrent in the 900 to 1500 nm region. Besides the n=1 excitonic type absorption, several absorption edges corresponding to higher quantization levels are observed. For InGaAs MQWs, the long wavelength photocurrent increases by increasing the number of wells from 10 to 20 and saturates for 30 periods. These results are qualitatively in good agreement with expected behavior. InGaAs/InP Quantum Well

The well compositions utilized for indium phosphide cells containing InAs, P_{1-x}, are x = 0.37 and x = 0.55 and x = 0.7, and...
they offer a set of MQW absorption edges at 1.1, 1.3, and 1.5 μm, respectively. However, as the As composition is increased in the well region, the lattice mismatch induced strain energy increases in the MQW. This excess of energy for thicknesses exceeding a threshold value called the “critical thickness” may result in the formation of dislocations and lead to a degradation of electronic properties.

In the absence of plastic relaxation the indium phosphide solar cells containing InAsP/InP MQW region are characterized by an increase of the short circuit current with respect to homojunction cells, as shown in Table 2, where the symbols have the following meanings: I sc is the short circuit current; V oc is the open circuit voltage; FF is the fill factor, which is defined as the ratio of the maximum power output divided by I sc x V oc; and η is the efficiency, which is electrical power output divided by incident power.

**TABLE 2**

<table>
<thead>
<tr>
<th>I-V characteristics without Antireflection Coating</th>
<th>I-region</th>
<th>I sc (mA/cm²)</th>
<th>V oc (Volts)</th>
<th>FF</th>
<th>η (AM1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>InP (p-n)</td>
<td>None</td>
<td>20</td>
<td>0.82</td>
<td>0.77</td>
<td>13.3%</td>
</tr>
<tr>
<td>InP (p-i-n)</td>
<td>0.3 μm undoped InP</td>
<td>20.2</td>
<td>0.75</td>
<td>0.74</td>
<td>12.5%</td>
</tr>
<tr>
<td>InP-MQW-10 period InAsP/InP</td>
<td>20 period InAsP/InP</td>
<td>28.2</td>
<td>0.56</td>
<td>0.67</td>
<td>11%</td>
</tr>
<tr>
<td>InP-MQW-20 period InAsP/InP</td>
<td>28.4</td>
<td>0.52</td>
<td>0.53</td>
<td>8.5%</td>
<td></td>
</tr>
</tbody>
</table>

For the InAsP-0.65P 0.35 well the short circuit current I sc increases with increasing number of periods up to 20 periods of MQW. For 30 periods, I sc decreased, indicating increased presence of dislocations in heterostructures having a large number of periods. It is difficult to draw conclusions on whether this current reduction is related to the decrease of minority carrier lifetime, associated with dislocations, or a more intrinsic phenomena.

The I-V characteristics of the MQW solar cells when compared to their conventional indium phosphide (p/n) counterpart is characterized by a systematic drop of the open circuit voltage (V oc). The open circuit voltage seems also to decrease by increasing the number of periods.

However, for several structures the relative increase of the short circuit current (I sc) is larger than the associated voltage drop. The efficiency of several MQW solar cells approached that of conventional solar cells, despite the decreased fill factor, FF. Typical I-V characteristics (under AM1 simulator) of a 10- and 20-period InAsP-0.65P 0.35/InP MQW solar cell is compared with its p-i-n counterpart in Table 2. For example, for a 10-period MQW cell, the I sc is improved by 30% while the voltage drop was 25%.

Furthermore, spectral response measurements shown in FIG. 4 of our best MQW InAsP/InP cells indicate a more efficient conversion for the photons located in the indium phosphide near band gap region (800-900 nm). Therefore, owing to an improved collection efficiency for photons having energy near the indium phosphide band gap energy, the MQW solar cell will be able to perform with a much thinner base than a conventional indium phosphide cell. This will have several advantages, including lower fabrication costs and less susceptibility to radiation damage.

It should be understood that n- and p-type layers described in this invention are reversible, i.e., the sequence can begin with either type and a change to the other type can occur at a homojunction or interface between layers. It should also be understood that the cells of this invention may be used as subcells in tandem solar cells.

The invention has been described with reference to its preferred embodiments. Those of ordinary skill in the art, may, upon reading this disclosure, appreciate changes or modifications which do not depart from the scope and spirit of the invention as described above or claimed hereafter.