

State-of-the-art of III-V Solar Cell Fabrication Technologies, Device Designs and Applications

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III-V solar cell technology is reviewed. Different fabrication processes for III-V semiconductor materials, cell designs and applications are presented. The two main growth techniques are molecular organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE), with growth control to a monolayer precision. This allows for growing heterostructures as multijunctions and quantum well solar cells, with a high theoretical efficiency. Applications in thermophotovoltaics (TPV), concentrator systems and space solar cells are outlined.

I. INTRODUCTION

This paper is devoted to the presentation of the state-of-the-art of III-V compound technology. Growth methods, types of cells and major applications are presented as obtained from the 17th Photovoltaic European Conference (2001). An international conference is the most suitable place to obtain information about the current research and technical trends.

The initial characteristics of III-V solar cells are excellent. Due to its direct bandgap electronic structure they are able to absorb 97% of the AM1 radiation in a thickness of $2\mu\text{m}$. Moreover, the precision of the growth methods that we will describe below allows for a high mobility of carriers, ensuring they can reach the junction before any recombination process takes place.

The main components for III-V are GaAs and InP , which can be alloyed with other materials as Al , Sb , to give rise to ternary or quaternary compounds, like $\text{Al}_x\text{Ga}_{1-x}\text{As}$ or $\text{In}_x\text{Ga}_{1-x}\text{As}_y\text{P}_{1-y}$. These compounds allow for a large flexibility in the design of devices, and therefore these cells can be used in different applications. The main parameter at our disposal is the size of the bandgap by selecting the relative proportion of elements in the compound. This allows for designing cells with small bandgap suitable for thermophotovoltaics (TPV), where infrared (IR) radiation is absorbed from a heat source or as sub-bandgap radiation not absorbed by an upper cell in a tandem junction, increasing the efficiency of the cell since the spectral response is larger.

Despite all these desirable characteristics the production of III-V semiconductors is expensive, hindering its massive use, and restricting them to specialist applications like TPV or solar concentrator. Si cells present an indirect bandgap in its crystalline form which requires a high purity of the crystal and thickness of the cell; the reported efficiencies are below the III-V systems. Polycrystalline or Amorphous Si solar cells are promising, however their efficiency are even lower, and not much room for improvement exists. Thin-film materials, CdTe , CdS or CuInS_2 , are still in research stages, although the thinness of the cells promise a reduction in cost for future cells, which would allow for easily competing with Si or III-V cells [1].

Section II presents in detail the different growth methods for III-V compounds. High-efficiency solar cell designs, as multijunctions and quantum wells are considered in section III. Section IV is devoted to a brief introduction of the main applications of III-V solar cells. Conclusions are presented in section V.

II. GROWTH METHODS OF III-V COMPOUNDS

Growing methods for III-V compounds can be divided in two categories: bulk growth methods, as Czochralski and Bridgman methods, or epitaxial growth methods, as liquid phase epitaxy (LPE), chemical vapor deposition (CVD), molecular organic chemical vapor deposition (MOCVD) or molecular beam epitaxy (MBE), which we will describe below. The main methods are described for the growth of GaAs , being this the most important compound of the group; all the other compounds, including ternary and quaternary compounds, are grown using the same techniques, and adding the necessary elements, Al , In , Sb , etc. in the required proportions. Elements used as n-type dopants are S , Se , Te , Sn , Si , C , Ge , and p-type dopants are Zn , Be , Mg , Cd , Si , C , Ge , where the last three ones act as n-type or p-type if they replace a Ga or a As atom in the crystalline structure.

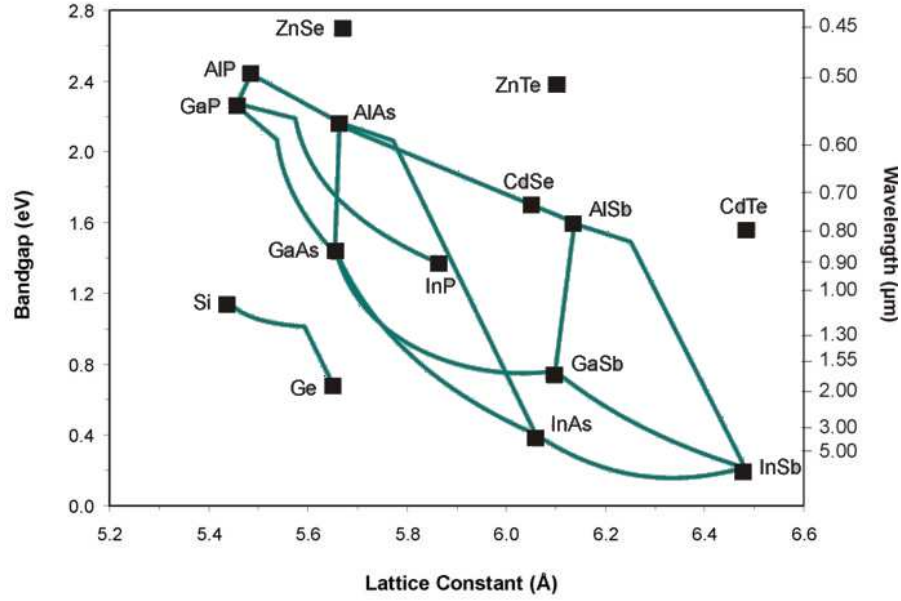


FIG. 1: Ternary and quaternary III-V compounds relation between lattice constant and bandgap.

A. Bulk growth methods

We will shortly describe here the two bulk growth methods for completeness of the presentation, since the most efficient structures manufactured based on III-V compounds use epitaxial growth methods [2, 3].

The Czochralski method grows the compound from the molten. A seed, with the desired crystalline structure is put in contact with the molten, and pulled out slowly enough for a crystal to grow on the seed. The boule is rotated to favor uniformity in temperature and compound density. The transition from the liquid phase to the crystalline phase ensures a purification of the residual impurities in the molten in agreement with their segregation coefficients. This is the main method used to grow silicon crystals.

The Czochralski method for growing single crystals of $GaAs$ must be modified due to the volatility of As at Ga melting point temperature ($1238^\circ C$), which would escape the molten. Then, the molten is covered with a 1 cm thick layer of boron trioxide B_2O_3 which, in conjunction with high pressure inert gas in the growing chamber, prevents the evaporation of As . This method is known as Liquid Encapsulated Czochralski (LEC) method. Doping elements or other III-V elements required for growing ternary or quaternary compounds can be added to the molten in order to obtain the desired proportion of elements in the compound.

Bridgman method is a two-zone technique, where a crucible of graphite is pulled from one side of a sealed tube made of quartz, at a temperature of $1242 - 1460^\circ C$, above Ga melting point, to the other side with a temperature of $610 - 620^\circ C$, to maintain the necessary overpressure of As . A seed of $GaAs$ is set at the coolest edge of the crucible to establish the crystal orientation.

B. Epitaxial growth methods

Epitaxy consist on the ordered growth of one crystal upon another, whose orientations are related and well defined. It could be a homoepitaxy, when growing a new layer of the same compound on top of the substrate, or heteroepitaxy, when the compound grown is different from the substrate.

In the case of III-V semiconductors these techniques allow for a wide range of electronic and optoelectronic properties influenced by the substrate. The introduction of ternary and quaternary compounds, as for example $Al_xGa_{1-x}As$ and $In_xGa_{1-x}As_yP_{1-y}$, offers even further possibilities. In Fig. 1 it is shown how Ge , $GaAs$ and $AlAs$ have roughly the same lattice constant with different bandgaps. Even in the case of lattice mismatch, elastic strained structures can be produced by slowly modifying the relative proportions of the elements of the compound, which is known as *graded substrate* ($GaP \rightarrow GaAs_xP_{1-x}$).

This can be achieved due to the low growing rates of epitaxial techniques which allows for flexibility in the selection

of the semiconductors used, its thickness, as well as the type and profile of the doping (due to the low temperature used in this methods the cross-diffusion of dopants and impurities is very reduced). Control over the growing process to one monolayer level offers the possibility of growing layered structures, known as *superlattices*, where layers of different compounds are grown upon each other with a thickness smaller than electronic mean-free path. All this allows for high purity compounds with high values of mobility, life-time and mean-free path for minority carriers.

The different methods using epitaxial growth are *liquid phase epitaxy* (LPE), *Chemical Vapor Deposition* (CVD), *Molecular Organic Chemical Vapor Deposition* (MOCVD), *Molecular Beam Epitaxy* (MBE), which are described next.

1. Liquid Phase Epitaxy (LPE)

This method deposits epitaxial layers from the liquid phase materials, and takes advantage of the fact that adding impurities to the molten reduces the melting point temperature (e.g. $GaAs + As$ melting point is lower than that for $GaAs$), and therefore the molten can be kept to a lower temperature such that the seed will not melt. The solution is cooled slowly and new epitaxial layers form on the seed of $GaAs$. Since the concentration of impurities in the liquid solution increases as the crystal grows it is necessary to further reduce temperature to continue the growing process. Therefore the epitaxial growth is controlled by the rate at which temperature is lowered. By growing the crystal from the liquid state the segregation of impurities ensure the high purity of the crystal.

2. Chemical Vapor Deposition (CVD)

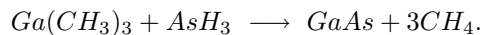
CVD is also known as Vapor Phase Epitaxy (VPE) and grows crystals from gaseous Ga and As compounds, which react on a substrate to form $GaAs$ at temperatures of about $650 - 850^\circ C$ [2, 3]. The whole process comprises several steps, first the reactants (gases and dopants) are transported to the substrate, then are transferred and absorbed into the substrate, where the chemical reaction catalyzed at the surface takes place and the layer is grown at rates of $1\mu m/h$. Finally the gaseous subproducts are desorbed to the gas stream and transported out of the reaction chamber. In the most elemental reaction $GaCl_3$ and As_4 are transported to the substrate with hydrogen H_2 , producing the reaction:



Chemical vapor deposition can be carried out at atmospheric pressure (APCVD) or at low pressure (LPCVD). At the same time the chemical reactions on the substrate can be enhanced by plasma (Plasma-Enhanced CVD) or by UV light (Photo-Enhanced CVD), where the substrate is heated by means of the ions in a plasma or ultraviolet light shed on its surface.

3. Molecular Organic Chemical Vapor Deposition (MOCVD)

MOCVD is a particular kind of CVD growth process characterized by the chemical nature of the precursors. Metalorganic compounds with relatively high volatility are used as precursors for both, main elements and doping elements. In this case trimethyl-gallium (TMGa) and arsine are carried by hydrogen at atmospheric pressure to the substrate, which is heated at $600 - 800^\circ C$ by radio frequency (RF) to produce the pyrolytic reaction [2-4]:



This technique gives very good results for phosphorous compounds, as InP , where $TMI n$ is used as precursor. It is also widely used for the production of quantum well (QW) structures and multijunctions [5], and gives very good results for atomic layer epitaxy (ALE) growth [6]. When photo-enhanced MOCVD is used the temperature can be kept below $200^\circ C$, which ensures a high quality of the material, with large values for the mobility, life-time and mean-free path of minority carriers.

Dopants are transported to the substrate in form of metallic compounds as well, for example dimethyl-zinc (DMZn), diethyl-zinc (DEZn), disilane (Si_2H_6), $DEBe$, $TESn$ or CCl_4 , are used as dopant precursors for different types of semiconductors [7].

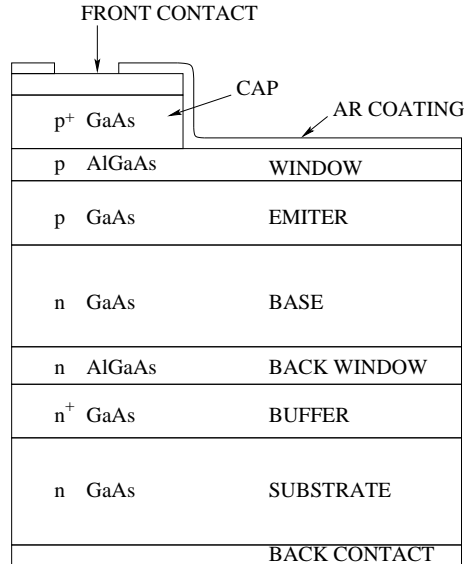


FIG. 2: Single junction heterostructure $p\text{-AlGaAs}/p\text{-GaAs}/n\text{-GaAs}$, introducing the window and buffer layers to minimize surface recombination processes and propagation of defects into the junction.

4. Molecular Beam Epitaxy (MBE)

MBE is a technique where a reaction of thermal gaseous beams of molecules from evaporation or sublimation of liquids or solids with a crystalline surface is produced under ultra-high-vacuum conditions to form the epitaxial layer [3, 4]. This vacuum conditions together with the highest standards of cleanness used in the construction of the techniques and apparatus allows for a high purity of the grown samples.

The reactants are evaporated from separated graphite effusion ovens (Knudsen cells), heated radiatively to the convenient temperature to adjust the evaporation rate (in particular an overpressure of As_4 is maintained to compensate its low sticking coefficient). To ensure the uniformity of the layers the substrate rotates once per monolayer grown. The growth rate of this technique is lower than for MOCVD ($< 1\mu\text{m}/h$). The ability to stop and start the beams in a shorter time than required for growing a layer allows for monolayer precision and unique doping profile in the growing process [8, 9].

When molecular organic compounds are used the method is called Molecular Organic MBE (MOMBE, also known as Chemical Beam Epitaxy, CBE). This allows for a uniform source flux over a large area. In the Gas Source MBE (GSMBE) gases are changed form outside the ultra-high-vacuum chamber, which makes the process more flexible [10].

III. THE QUEST FOR HIGH-EFFICIENCY SOLAR CELLS

Since the fabrication of the first $GaAs$ cell in 1956, with an efficiency of 4%, a steady effort to improve the efficiency of the cells has been undertaken achieving efficiencies in the range of 20-30%. Improvements in all the areas have been implemented in order to reach and overpass these efficiency rates: surface and edge passivation and masking layers as SiO_2 , Si_3N_4 , or antireflexion (AR) coatings Sb_2O_3 or ZnS/MgF_2 [11]; layers width reduction to minimize serial resistance, and control of the doping level in the $p/n\text{-GaAs}$ layers to increase the open circuit potential without reducing the long carrier diffusion length are some of them.

The phase diagram in Fig. 1 shows the relation of the bandgap and lattice constant for several III-V ternary and quaternary compounds, and the transitions between them for variations in the relative proportions in their elements, e.g. $Al_xGa_{1-x}As$. Therefore it is possible to use the phase diagram to lattice match different heterostructure compounds grown by MOCVD or MBE methods, which allow for control of the growing process to a single layer. This is known as *bandgap engineering*, and will reduce the recombination processes in the interphase [7, 12].

In the case of the single junction $GaAs$ solar cell shown in Fig. 2 a *window* layer of $AlGaAs$ was grown at the top of the cell, with a larger gap than $GaAs$ (buried homojunction). This avoids the absorption of photons too close to the front surface leading to large surface recombination processes. A similar one can be sited at the bottom of the cell producing the back surface field (BSF) [12]. The lattice match of the whole range of compounds $Al_xGa_{1-x}As$

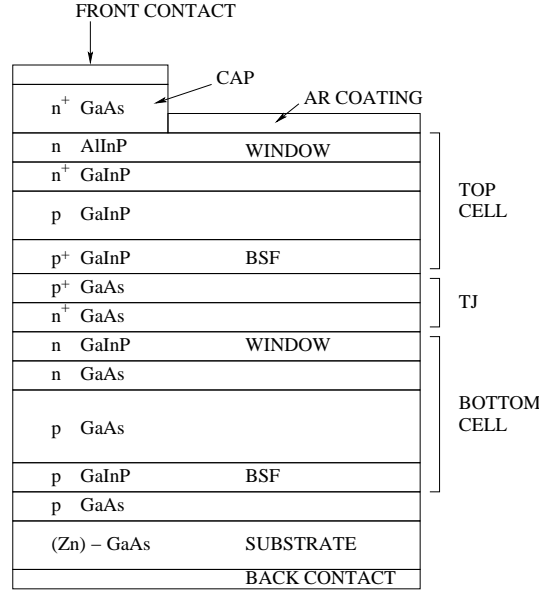


FIG. 3: Layer structure of a multijunction. It shows two similar structures for the top and bottom cells, with window and back surface field (BSF) layers, and joined together by two layers or $GaAs$ (TJ, tandem junction).

is excellent, as it can be appreciated in Fig. 1, avoiding interphase recombination. A buffer layer is also introduced between the substrate and the active region of the cell to reduce the propagation of defects.

A. Multijunctions and tandem cells

Despite all the progress achieved in the fabrication of III-V solar cells there is an intrinsic source of efficiency reduction coming from the lost of sub-bandgap energy photons, which are not absorbed into the cell. One of the approaches to this problem is the construction of multijunction cells, which consist of devices involving more than one solar cell, in such a way that the higher energy radiation is absorbed by a larger bandgap solar cell, and the residual low-energy solar radiation is absorbed by a smaller bandgap solar cell [2, 7].

The absorption of different wavelength radiation by different devices can be achieved by an optical beam splitter, by a mechanically stacking two or more solar cells, with reduced bandgap as we go down in the stack, or by a monolithic multijunction structure grown by MOCVD or MBE. For mechanically stacked solar cells we can use a $GaAs$ solar cell ($E_g = 1.4eV$), and a $GaSb$ solar cell ($E_g = 0.7eV$) [7].

The structure of a monolithic multijunction solar cell is shown in Fig. 3, where we can appreciate the repetition of the structure for the two different cells, where the $GaInP$ -based cell must have a larger gap than the $GaAs$ -based one. A substrate of $GaAs$ makes lattice matching compatible, however other crystals as Ge or Si would be interesting in order to reduce price. Ge is a lattice matching with $GaAs$, however Si has better mechanical properties. We could grow the $GaAs$ cell on Si [100] crystalline planes and a deviation of 4° , or growing a strained semiconductor [4]. The best option is to grow a linearly graded Si_xGe_{1-x} alloy to reduce the strain in the interphase [12, 13]. A more novel technique is known as *epitaxial lift-off* (ELO), which enables the separation of the substrate for its future reuse by selective wet etching of a sacrificial layer, deposited between the substrate and the actual solar cell structure. A sacrificial $Al_{0.7}Ga_{0.3}As$ release layer ($5\mu m$) is etched by a HF solution [14].

Triple and quadruple-junctions have a theoretical efficiency of 30% and 40% due to its broader spectral response [15, 16]. The external quantum efficiency (EQE) for a triple-junction is shown in Fig. 4. The lower lines represent the individual cell efficiencies, which are chosen for a different range of the spectrum, and we can see how the total efficiency of the junction (the highest curve) is largely increased when they are added up together.

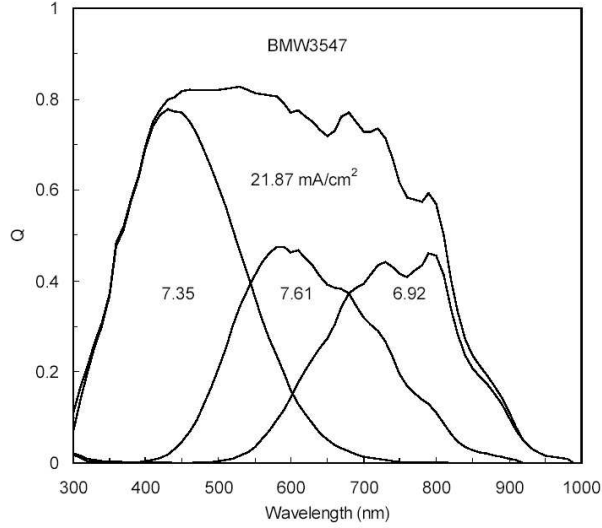


FIG. 4: External Quantum Efficiency for a triple-junction solar cell.

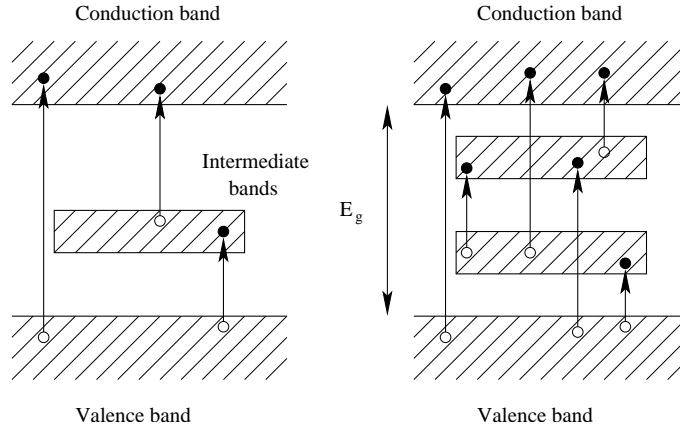


FIG. 5: Intermediate band solar cell. The presence of deep traps in the bandgap of the semiconductor allows for the interband excitation of electron-hole pairs with sub-bandgap energy.

B. Quantum well solar cells

Another approach to the absorption of sub-bandgap energy photons is the construction of a n-i-p junction with a high concentration of deep impurities in the intrinsic region, leading to the formation of one or several intermediate bands as shown in Fig. 5. Since the gap of the junction, E_g , is not modified, the open circuit potential remains unchanged. At the same time these intermediate bands allow for lower energy photons to be absorbed, and the pairs cannot decay thermally because of the discrete character of the multibands [8, 17, 18]. While an homojunction limiting efficiency is 40.7%, triple-band multiband efficiency is 63.2%, and quadruple-band multiband efficiency reaches 71.7%. The higher the number of intermediate bands the higher the efficiency of the device, reaching the 86.8% in the limit of infinite number of bands [15, 19].

IV. III-V SOLAR CELL APPLICATIONS

GaAs and other III-V semiconductors present high quality properties: a direct bandgap with high absorption, relatively insensitivity to temperature, and radiation resistance. These properties make them suitable for three major applications: thermophotovoltaics (TPV), concentrator systems, and space applications [6, 9].

A. Thermophotovoltaic systems (TPV)

Thermophotovoltaics stands for the conversion of infra-red (IR) radiation into electricity. This could be achieved with small bandgap solar cells ($0.4 - 0.7\text{eV}$) as *GaSb* homojunctions or more sophisticated heterojunctions [20, 21] exposed to radiation from a source below 2000°C . The use of such devices allows for a maximally efficient conversion of fossil fuels or waste heat into electricity [15]. This technology can be transferred to concentrator systems to absorb the IR part of the spectrum in tandem structures or multijunctions [7]. QW are also suitable for absorbing IR radiation due to the existence of intermediate bands [5, 22].

B. Concentrator systems

One of the major expectations under development is the use of concentrators to increase the number of carriers, together with some of the technologies described in the previous section, which would lead to high efficiencies, with present values in the range of 26-27% [16] or even approaching 34% [23, 24]. The use of tandem cells and multijunctions is essential for reaching such efficiencies as it is perceived from current R&D trends [12]. Concentration systems report efficiencies above 30%, for example Ballard reports a 33.5% efficiency for a triple-junction under $C = 308$ [5]. Even homojunctions can reach such high-efficiency values, as a *GaAs/AlGaAs* homojunction efficiency close to 30% for $C = 1000$ [25].

C. Space systems

III-V solar cells are important for space applications due to its high-efficiency conversion and good radiation resistance that its thinness provides, reducing the probability of radiation damage [12]. The main effort in space solar cells is devoted to reduction of radiation damage. Although high-efficiency tandem solar cells with 3, 4 and 5-junctions have been reported by Dimroth [16].

V. CONCLUSIONS

We have presented an account of III-V semiconductor compounds state-of-the-art regarding growth methods, high-efficiency devices and major applications as presented in the 17th Photovoltaic European Conference held in 2001. The most used growth methods are MOCVD and MBE, which allow for the fabrication of monolayer controlled structures and quantum wells, and control over doping profiles. Heterostructures can be used to grow multijunctions, making possible the absorption of sub-bandgap radiation, which increases the spectral response of single cells. The main applications of III-V semiconductors is in TPV and concentration systems, where efficiencies over 30% have been reported. Space solar cells are also constructed with III-V compounds due to their radiation endurance.

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- [1] A. Goetzberger, *Solar cell material and technology: From the past to the future*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 9.
 - [2] Richard H. Bube, *Photovoltaic Materials*, (Imperial College Press, 1998).
 - [3] S. M. Sze, *Semiconductor Devices, Physics and Technology*, (John Wiley & Sons, 1985).
 - [4] R. A. Stradling and P. C. Klipstein, *Growth and Characterisation of semiconductors*, (Adam Hilger, Bristol and New York, 1990).
 - [5] I. Ballard *et al.*, *The effect of temperature on the efficiency of multi quantum well cells for solar and thermophotovoltaic applications*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 41.
 - [6] C. Agert *et al.*, *Novel device structures for infrared solar cells based on GaAs pn-homojunctions, pn-heterojunctions, and tandem cells*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 372.
 - [7] A. W. Bett *et al.*, *Development of high-efficiency mechanically stacked GaInP/GaInAs–GaSb triple-junction concentrator solar cells*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 84.
 - [8] R. Songmuang *et al.*, *Photovoltaic effects in composite quantum dot structures*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 174.
 - [9] M. Ružinský *et al.*, *Photovoltaic and dielectric measurements on selected GaAs/AlGaAs solar cells for concentration applications*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 292.
 - [10] S. Laaksonen *et al.*, *Gas-source molecular beam epitaxy of GaAs on Ge for solar cell applications*, Proceedings of the 16th European Photovoltaic Solar Energy Conference (James & James Ltd.) (2000) 955.
 - [11] D. Martín and C. Algora, *GaSb thermophotovoltaic converters manufactured by single zinc diffusion using spin-on masking layers*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 152.
 - [12] M. Yamaguchi, *Present status of R&D super-high-efficiency III-V compound solar cells in Japan*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 2144.
 - [13] D. B. Brushnell *et al.*, *GaAsP/InGaAs strain-balanced quantum well solar cells*, Proceedings of the 16th European Photovoltaic Solar Energy Conference (James & James Ltd.) (2000) 999.
 - [14] M. M. A. J. Voncken *et al.*, *III/V epitaxial lift-off, investigated by multi-release layers*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 121.
 - [15] M. A. Green, *Third generation photovoltaics: Recent theoretical progress*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 15.
 - [16] F. Dimroth *et al.*, *Next generation GaInP/GaInAs/Ge multi-junction space solar cells*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 2150.
 - [17] L. Cuadra *et al.*, *Strain considerations for the design of the quantum dot intermediate band solar cell in the $Ga_xIn_{1-x}As/Al_yGa_{1-y}As$ material system*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 98.
 - [18] A. Luque, A. Martin and L. Cuadra, *High efficiency solar cell with metallic intermediate band*, Proceedings of the 16th European Photovoltaic Solar Energy Conference (James & James Ltd.) (2000) 59.
 - [19] A. S. Brown and M. A. Green, *Limiting efficiency of multiple band solar cells: an overview*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 246.
 - [20] G. J. Conibeer *et al.*, *Towards a GaAs – InAs tandem junction TPV cell*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 269.
 - [21] J. Toušková *et al.*, *Transport mechanism and spectral characteristics of GaSb/GaAs heterostructures prepared by MOVPE*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 146.
 - [22] J. P. Connelly *et al.*, *Modelling multi quantum well solar cell efficiency*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 204.
 - [23] L. M. Fraas *et al.*, *34% efficient InGaP/GaAs/GaSb cell-interconnected-circuits for line-focus concentrator arrays*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 2300.
 - [24] L. M. Fraas *et al.*, *30% efficient InGaP/GaAs/GaSb cell-interconnected-circuits for line-focus concentrator arrays*, Proceedings of the 16th European Photovoltaic Solar Energy Conference (James & James Ltd.) (2000) 929.
 - [25] C. Algora, I. Rey-Stolle and E. Ortiz, *Towards 30% efficient single junction GaAs solar cell*, Proceedings of the 17th Photovoltaic European Conference (WIP-Munich and ETZ-Florence) (2001) 88.