Novel semiconductors for sustainable solar energy technologies

F A Ponce
Department of Physics, Arizona State University, Tempe, AZ 85123, USA
E-mail: ponce@asu.edu

Abstract. Novel materials must be found in order to develop advanced sustainable solar energy technologies. This paper presents recent research being pursued by my group at Arizona State University in the study and development of III-V semiconductors for improving the efficiency of photovoltaic devices beyond the Shockley-Queisser limit. Although in the early stages of development, significant advances are happening in two directions described here. One is for intermediate-band solar cells, using InAs quantum dots in wide gap III-V semiconductor thin films. The other is for double-junction InGaN solar cells for high-temperature applications. The theoretical efficiencies of these two systems resemble that of triple-junction cells, at above 60%.

1. Introduction
We are experiencing vital challenges associated with climate change. It is clear that human activity is seriously affecting the atmosphere leading to increase in the temperature of the earth’s surface, affecting among many other aspects, the thermal stability of our planet. This is believed to be due to very rapid technological developments in the last hundred years that have relied on extensive use of fossil fuel. Communication technologies such as television and the internet have exposed the fast development in technologically advanced societies to the rest of the world, and thus have greatly increased the demand for energy. The rapid pace of global warming presents us with life-or-death challenges [1,2].

There is an urgent need to develop a non-polluting and sustainable approach to the use and generation of energy. A first step is to find ways toward efficient use of energy. For example, the development of GaN-related semiconductors in the past 25 years have led to the current white LEDs that are becoming the standard for illumination, with huge savings in energy [3,4]. The efficiency of white LEDs has reached 300 lumens per watt in the laboratory in 2015, and worldwide implementation is expected to have a large impact in lessening the demand for electric energy [5,6].

Another important challenge is in the development non-polluting, renewable energy sources, such as photovoltaic solar cells that converts the energy of light into electricity. The photovoltaic effect was demonstrated by Edmond Becquerel in 1839. The physical principles were explained in a 1905 paper by Albert Einstein, for which he won the 1921 Nobel Prize in Physics. Researchers at Bell Laboratories produced the first practical photovoltaic cell in 1954, with a reported efficiency of 6% [7]. Shockley and Queisser showed that a single p-n junction solar cell should have a maximum efficiency of 30%, for an energy gap of 1.1 eV [8]. Such ideal band gap value closely corresponds to silicon. This maximum efficiency results from a balance between the absorbed light (photons with energies above the band gap), the energy lost as the excited carriers relax to the semiconductor band edges, and the light not absorbed by the device (photons with energies below the band gap). Much effort has been made to achieve the predicted maximum efficiency. Carrier recombination at surfaces, contact interfaces, and in the bulk...
had to be minimized. In 1998 a 22.8% silicon solar cell efficiency was demonstrated [9]. The current record efficiencies for silicon solar cells is at about 26% [10].

Solar irradiation varies significantly around the world. In the American continent, regions of maximum solar energy irradiation are centered around Peru in South America and around Arizona in North America, as shown in figure 1 [11].

Figure 1. World solar energy map [11].

The conversion efficiency can be significantly improved with the use of p-n diodes with different bandgaps stacked in a sequence from highest to lowest bandgaps. The purpose is to minimize the thermal losses associated with relaxation of carriers excited much above the semiconductor band gap down to the band edges for collection by the p-n junction. Table 1 shows the expected values for multi-junction solar cells operating under one sun irradiation, as well as for operation under maximum solar concentration. A GaInP/GaInAs/Ge triple-junction solar cell was reported in 2007 to have surpassed 40% efficiency [12].

Table 1. Efficiencies for multijunction solar cells operating under one sun exposure, and under maximum solar concentration conditions.

| # of junctions in solar cells | Efficiency (%) (1 sun) | Efficiency (%) (Max conc.) |
|------------------------------|------------------------|----------------------------|
| 1                            | 30.80                  | 40.80                      |
| 2                            | 42.90                  | 55.70                      |
| 3                            | 49.30                  | 63.80                      |
| ∞                            | 68.20                  | 86.80                      |

In addition to the difficulties encountered in the single-junction case, multi-junction solar cells have to deal with issues such as lattice mismatch (for materials with different lattice parameters), thermal...
mismatch (different thermal expansion coefficients), and the production of tunnel junctions to allow non-resistive transport between p- and n-type layers of different materials.

Two alternatives to the triple junction concept are presented in this paper, which involve interesting physical concepts. One is the use of semiconductors with states in the bandgap that produce an intermediate band. The intermediate band introduces two sub-band absorption stages that together with the matrix resemble a triple-junction solar cell. Another one is a high-temperature hybrid thermal-photovoltaic model consisting of a double-junction solar cell made of InGaN alloys that operates at temperatures above 400 °C, in a design that in addition to the light generated current stores heat generated by the cells as well as heat from the transmitted infrared radiation (not absorbed by the cells) for utilization during dark conditions. When successful, these two options should have efficiencies above 60%. However, they currently are in the early stages of development.

2. Intermediate-band solar cells (IBSCs)
IBSCs have been proposed in order to overcome the Shockley-Queisser limit of single-junction solar cells [13]. This is achieved by introducing high density of states in the semiconductor bandgap to form an intermediate band (IB), which allows transitions from the valence band (VB) to the IB, and from the IB to the conduction band (CB), as shown in figure 2(a) [14].

The introduction of the intermediate band allows the absorption of light for energies below the semiconductor band gap, which otherwise would not contribute to the solar cell efficiency. Therefore, in addition to absorption across the semiconductor band gap (E_G), absorption by E_M and E_L will add to the photovoltaic current. The optimum values of E_G = 1.95 eV, E_M = 1.24 eV, and E_L = 0.71 eV are expected to result in a 63% efficiency under full sun concentration [14].

InAs quantum dots (QD) grown on Al_{0.3}Ga_{0.7}As and Ga_{0.5}In_{0.5}P have been found to have characteristics appropriate for IBSCs. InAs grows on GaAs as lens-shape islands, following the Stranski-Krastanov model. Island growth is due to strain energy resulting from lattice mismatch, that can be minimized by formation of the extra surface (compared with 2-D growth). Therefore, control of the island size becomes critical in the design of the IBSCs, as shown in figure 2(b) [14,15].

![Figure 2. Theoretical model of an intermediate-band solar cell structure. (a) Band energy diagram showing the three different energy transitions for the IBSC. (b) Transition energies at room temperature as a function of the QD height for InAs QD/Al_{0.3}Ga_{0.7}As (squares) and GaAs (circles). The horizontal dashed lines indicate the ideal energy values for the IBSC applications. The horizontal solid lines indicate the Al_{0.3}Ga_{0.7}As and GaAs energy gaps [14].](image-url)
Figure 3. Two-beam diffraction-contrast bright-field TEM images of InAs QDs under $g = 220$.
(a) Large, relaxed QD showing moiré fringes associated with misfit dislocations. (b) Small, strained QD showing Ashby-Brown contrast [16].

Figure 4. Equilibrium force calculation of the critical thickness as a function of lattice mismatch, for a single dislocation dipole and for a periodic array of dislocation dipoles. Inset: simplified model used to determine the critical thickness [16].

Figure 5. (a) Photoluminescence (PL) spectra for relaxed QDs (red) and for strained QDs (blue). (b) QD PL spectra of relaxed QDs for excitation power densities of 0.5 and 6.4 mW, indicating ground and excited QD states [16].

Figure 6. Size distribution in a single QD layer. (a) Plan-view bright-field image. (b) Lateral size distribution of 189 QDs extracted from plan-view TEM image, with binning size of 3 nm [17].
Dislocations are detrimental to the electronic properties of InAs QDs [16]. At a critical island size, plastic relaxation occurs with the generation of misfit dislocations as in figure 3(a). Small QDs are fully strained and exhibit strain-related Ashby-Brown contrast in TEM images, as in figure 3(b). Strain relaxation occurs by generation of misfit dislocation loops around each QD [16]. The critical thickness for strain relaxation depends on the dimensions of the QD, and in particular on the height, as shown in figure 4. For the case of InAs/GaAs, with a lattice mismatch of 6.9 %, the critical height is about 5 nm. For a height below that value the dislocation line tension is larger than the strain energy, and the dislocation loops collapse, resulting in a fully strained quantum dot. Photoluminescence measurements show optical activity for strained InAs QDs, and no activity for relaxed QDs, see figure 5(a). The QD emission typically consists of two peaks, representing the ground and excited states, see figure 5(b).

Size plays an important role in the energy level, see figure 6. Ideal conditions should occur to obtain uniform QD sizes. Height is dominant in producing the ground state in the QD, since it is the smaller dimension for lenticular QD shapes. There is an approach that yields similar heights for QDs in a layer, consisting of partially capping the layer of QDs, in our case with GaAs, and then annealing at high temperatures. The technique is also called indium-flushing. The result is that the exposed top of the QD diffuses laterally producing a spool shape, with the QD bound by two thin disks, above and below [17], producing QDs with height similar to the thickness of the capping layer.

An alternative approach is to use Ga_{0.5}In_{0.5}P (GaInP) as the semiconductor matrix. It has a bandgap close to the ideal value of 1.95 eV for IBSCs, and is currently being explored with InAs QDs for the

![Figure 7](image-url)
intermediate band. One important aspect of GaInP is its tendency towards CuPt ordering of the group III elements, which is observed to vary during growth by metalorganic vapor-phase epitaxy of InAs quantum dots capped with GaAs in a GaInP matrix. The room-temperature value of the band gap is 1.90 to 1.92 eV for the disordered phase, and 1.83 to 1.85 eV for the ordered phase. Ordering in GaInP is observed only along the [110] crystal direction. Such orientation can easily be identified using high-angle annular dark-field (HAADF) STEM imaging, as shown in figure 8. While GaAs exhibits a close to symmetric dumbbell structure corresponding to the Ga-As columns in the [110] projection (Ga and As have similar atomic numbers, 31 and 33), the Ga/In-P dumbbells are quite asymmetric (Ga, In, P have different atomic numbers, 31, 49, 15), and appear as tear-drops point either up or down depending of the polarity, as seen in the figure. We use this technique to identify the right projection for observation of ordering. The monolayer superlattices are formed along [111] or [111] directions. They are observed in TEM along the [110] projection, with the group-V element positioned above the group-III elements in the dumbbell configuration. Ordering happens when the larger group III elements (Ga and In) arrange themselves along a {111}A plane, and the smaller group V element (P) on the next {111}B plane. Ordering is best observed using HAADF, and also using standard STEM imaging techniques as shown in Fig. 9, where ordering produced in the presence of spool-shaped InAs QDs [17].

While ordering is not affected by the insertion of a GaAs layer, the growth of InAs quantum dots capped with GaAs results in fully ordered, partially ordered, or fully disordered GaInP. We have observed that the degree of ordering depends on the deposition time of the InAs quantum dots and on the thickness of the GaAs capping layer. Our results indicate that disordered GaInP occurs in the presence of excess indium at the growth surface, which is necessary for growth of strained InAs quantum dots. Ordering resumes when the excess indium is consumed.

Figure 8. (left) HAADF images of the InGaP/GaAs interface region taken along two perpendicular projections for polarity determination [19].

Figure 9. (right) HAADF and HRTEM images of spool-shape QDs, showing ordering in the GaInP layer [19].
3. \( \text{In}_x \text{Ga}_{1-x} \text{N} \) solar cells for high-temperature applications

The group III nitrides (alloys of the AlGaInN family) have become very important for many technological applications. Solid state lighting is one of the most important ones. The blue LED, based on InGaN, was developed and commercialized in the early 90’s, and was turned into white LEDs with the addition of phosphors to convert blue into a spectrum resembling white light. Today, it is becoming the primary source for artificial illumination. These materials were first developed in the early 70’s, Jacques Pankove being the pioneer who worked alone for many years. In the mid 80’s, Isamu Akasaki and Hiroshi Amano demonstrated methods to produce high quality GaN thin films, and the ability to control doping, which in 1989 demonstrated p-type GaN. In the early 90’s, the Nichia Corporation team led by Shuji Nakamura developed commercial methods for the production of LEDs, these included the use of low temperature GaN buffer layers and thermal annealing for p-type activation. Soon followed InGaN quantum wells for high efficiency LEDs [4]. The evolution of lighting technology with time is shown in Fig. 10. The 2014 Nobel Prize in Physics was awarded to Akasaki, Amano, and Nakamura, in recognition for their contributions to the efficient use of energy for illumination [3].

![Figure 10](https://example.com/figure10.png)

**Figure 10.** Evolution of visible LEDs. Over the past have century, the arsenide, phosphide, and nitride semiconductors have produced LEDs with quantum efficiencies that are currently very close the physical limit for conversion of electricity into light (Adapted from Ref. 4).

The nitride semiconductors have unique properties: Their bandgap extends from infrared to ultraviolet (\( E_g = 0.65 \text{ eV for InN}, 3.4 \text{ eV for GaN}, \text{ and } 6.2 \text{ eV for AlN} \)); which includes the full visible range. The range for InGaN alloys includes the solar spectrum (See figure 11), which closely resembles blackbody radiation at 5,500 °C. The microstructure of these materials include high densities of dislocations, which are necessary for growth of these strongly bonded materials [20]. The crystal structure lacks a center of symmetry, which results in strong polarization properties, both spontaneous as well as piezoelectric (resulting from the strain due to lattice mismatch that can be up to 11%) [21].

The nitrogen bond requires high temperatures for growth of these materials (1050 °C for GaN). This means that devices made of these materials should be able to operate at high temperatures for long periods of time.
Figure 11. Solar spectrum (right) and the bandgap energy for Ga\textsubscript{x}In\textsubscript{1-x}N alloys.

Figure 12. It is now possible to covert electricity into light, with close to the physical conversion limits. The challenge is now to convert light (from the sun) in to electricity with equal efficiency.
The main challenge has been associated with the large lattice mismatch in InGaN/GaN at high indium compositions, which can range up to about 11%. A main limitation is the absence of easy-glide slip systems in the hexagonal wurtzite structure of these materials compared to the most common cubic zincblende structure. Because growth of high quality films happens perpendicular to the basal plane, which is also the easy-glide system, biaxial strain cannot be relieved by introduction of misfit dislocation from the growth surface. Thus, misfit strain energy can build up to high levels. In addition to the basal plane, slip can also occur along prismatic and pyramidal planes, but only at high strain energy levels. Experimentally we have observe that for indium compositions $x$ above 0.15, poor growth surface morphology results in high densities of defects, reaching a maximum at about 0.4, but then, for $x = 0.60$ and above, the film relaxes after a few monolayers, and growth occurs with few defects present, as observed in figure 13. The explanation for this phenomenon is in the nature of the critical thickness curve in figure 14. The critical thickness is seen to diminish with indium composition and reaches the range of interatomic distances at about $x = 0.5$.

![Figure 13](left) Cross-section TEM images of InGaN films with $[\text{In}] = 0.22$ to 0.66, taken along a $\langle 11\overline{2}0 \rangle$ projection, with $g = 1\overline{1}00$. Notice that the crystalline quality of the films improves with indium composition in spite of the increase in lattice mismatch. The misfit strain relaxation is observed as moiré fringes at the InGaN/GaN interface [22].

![Figure 14](right) Variation of the critical thickness for plastic relaxation associated to lattice misfit strain for InGaN/GaN with indium composition. The curves have been obtained using various models. The critical thickness of one lattice period happens at about $x = 0.55$ [22].
Using these concepts, refractory InGaN solar cells have been produced for high temperature applications [23,24]. The long term object is to build hybrid thermo-photovoltaic plants where double-junction InGaN-based solar cells can be operated under high concentration (figure 15). The heat generated either by thermal losses due to the limits in solar cell efficiency or by infrared light absorbed light absorbed at the base of the devices is absorbed by a fluid filled thermal receiver for storage and use at night.

Figure 15. Double-junction InGaN-based tandem solar cell (left), for absorption in the ranges 2.4 to 2.9 eV and 1.5 to 2.1 eV, for operation under high concentration (right) at temperatures up to 450 °C. The heat generated from thermal losses and solar light absorption in the infrared is stored via a molten salt duct for utilization during dark hours.

In summary, two methods to potentially improve the efficiency limits of current solar cell technology have been discussed. These concepts are equivalent to those of multijunction solar cells, and hold a promise to advance the current state of technology.

References
[1] Gore A 2006 An Inconvenient Truth (Emmaus, Pennsylvania: Rodate Press)
[2] Gore A 2013 The Future. Six drivers of global change (New York: Random House)
[3] Akasaki I Blue Light: A fascinating journey (Nobel Lecture) 2015 Angewandte Chimie-International Edition, 54, 7750-63
[4] Ponce F A, and Bour D P 1997 Nitride-based semiconductors for blue and green light emitting devices Nature 386-51
[5] Tsao J Y, Coltrin M E, Crawford M H, and Simmons J A 2010 Solid-state lighting: An integrated human factors, technology, and economic perspective Proc. IEEE 98 1162-79
[6] Feezell D, and Nakamura S 2018 Invention, development and status of the blue light-emitting diode, the enabler of solid state lighting Comptes Rendus Physique 19 113-33
[7] Chapin D M, Fuller C S, and Pearson G L 1954 A new p-n junction photocell for converting solar radiation into electrical power J. Appl. Phys. 676-7
[8] Shockley W, and Queisser H A 1961 Detailed balance limit of efficiency of p-n junction solar cells J. Appl. Phys. 510-9
[9] Blakers A W, Wang A, Milne A M, Zhao J, and Green M A 1989 22.8% efficient silicon solar cell, Appl. Phys. Lett. 55 1363-5
[10] https://en.wikipedia.org/wiki/File:Best_Research_Cell_Efficiencies.png, 2018 June 7
[11] Raza M Q, Nadarajah M, and Ekanayake C 2016 On recent advances in PV output power forecast Solar Energy 136 125-44
[12] King R R, Law D C, Edmondson K M, Fetzer C M, Kinsey G S, Yoon H, Sherif R A, and Karam N H 2007 40% efficient metamorphic GaInP/GaInAs/Ge multijunction solar cells Appl. Phys. Lett 90 183516-3
[13] Luque A and Martí A 1997 Increasing the efficiency of ideal solar cells by photon induced
transitions at intermediate levels Phys. Rev. Lett. 78 5014-7
[14] Jakomin R, Kawabata R M S, Mourão R T, Michá D N, Pires M P, Xie H, Fischer A M, Ponce F A and Souza P L 2014 InAs quantum dot growth on AlGaAs by MOVPE for intermediate band solar cells J. Appl. Phys. 116 093511-7
[15] Torelly G, Jakomin R, Pinto L D, Pires M P, Ruiz J, Caldas P G, Prioli R, Xie H, Ponce F A, Souza P L 2016 Early nucleation stages of low density InAs quantum dots nucleation on GaAs by MOVPE J. Crystal Growth 434 47-54
[16] Xie H, Prioli R, Fischer A M, Ponce F A, Kawabata R M S, Pinto L D, Jakomin R, Pires M P and Souza P L 2016 Improved optical properties of InAs quantum dots for intermediate band solar cells by suppression of misfit strain relaxation J. Appl. Phys. 120 034301-6
[17] Xie H, Prioli R, Torelly G, Liu H, Fischer A M, Jakomin R, Mourão R, Kawabata R M S, Pires M P, Souza P L, and Ponce F A 2017 Correlation between size distribution and luminescence properties of spool-shaped InAs quantum dots Semiconductor Sci. Techn. 32 055013
[18] Weiner E C, Jakomin R, Michá D N, Xie H, Su PY, Pinto L D, Pires M P, Ponce F A, and Souza P L 2018 Effect of capping procedure on quantum dot morphology: Implications on optical properties and efficiency of InAs/GaAs quantum dot solar cells Solar Energy Materials & Solar Cells. 178 240-8
[19] Ponce F A 2017 Microstructure and polarization properties of III-N semiconductors, Handbook of GaN Semiconductor Materials and Devices, W. Bi, H. Kuo, P.-C. Ku, and B. Shen, eds., chapter 2, 53-86 (Taylor & Francis Ltd., CRC Press, UK)
[20] Su P Y, Liu H, Kawabata R M S, Weiner E C, Jakomin R, Pires M P, King R R, Souza P L, and Ponce F A 2018 Effect of InAs quantum dots capped with GaAs on ordering in GaInP in press
[21] Ponce F A 2011 Electrostatic energy profiles at nanometer-scale in group III nitride semiconductors using electron holography Ann. Phys. 523 75-86
[22] Fischer A M, Wei Y O, Ponce F A, Moseley M, Gunning B, and Doolittle W A 2013 Highly luminescent, high-indium-content InGaN film with uniform composition and full misfit-strain relaxation Appl. Phys. Lett. 103 131101-4
[23] Williams J J, McFavilen H, Fischer A M, Ding D, Young S, Vadiee E, Ponce F A, Arena C, Honsberg C B, and Goodnick S M 2016 Development of a high-band gap high temperature III-nitride solar cell for integration with concentrated solar power technology Conf. Rec. IEEE 44th Photovoltaic Specialists Conf. 0604-7
[24] Williams J J, McFavilen H, Fischer A M, Ding D, Young S, Vadiee E, Ponce F A, Arena C, Honsberg C B, and Goodnick S M 2017 Refractory InGaN solar cells for high-temperature applications IEEE J Photovolt. 7 1646-52