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# Six not-so-easy pieces in intermediate band solar cell research

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**Abstract.** The concept of intermediate band solar cell (IBSC) is, apparently, simple to grasp. However, since the idea was proposed, our understanding has improved and some concepts can now be explained more clearly than when the concept was initially introduced. Clarifying these concepts is important, even if they are well known for the advanced researcher, so that research efforts can be driven in the right direction from the start. The six pieces of this work are: Does a miniband need to be formed when the IBSC is implemented with quantum dots? What are the problems for each of the main practical approaches that exist today? What are the simplest experimental techniques to demonstrate whether an IBSC is working as such or not? What is the issue with the absorption coefficient overlap and the Mott's transition? What would the best system be, if any?  [DOI: 10.1117/1.JPE.3.031299]

**Keywords:** intermediate band solar cells; next generation solar cells; quantum dots.

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## 1 Introduction

Since, the intermediate band solar cell (IBSC) was proposed,[1] it has generated some "frequently asked questions." In this article, we take the opportunity to review six of these and try to provide a clear answer to each of them. To undertake this task, it will be useful to briefly go over the fundamentals of the IBSC operation. In this respect, Fig. 1 shows the structure of a cell of this kind and its simplified bandgap diagram. The structure consists of an intermediate band (IB) material sandwiched between two conventional semiconductors, one p-type and the other n-type. The IB material is characterized by a collection of energy levels (the IB) located inside the semiconductor forbidden band thus dividing the bandgap, $E_G$, into two sub-bandgaps, $E_L$ and $E_H$, which are not necessarily equally spaced.

In equilibrium, the Fermi level, $E_F$, crosses the IB and, if the IB material is sufficiently thick as in the case illustrated, the IB material is located in a flat-band region. The Fermi level crossing the IB implies that this band is partially filled with electrons so that it has both electrons to be promoted to the conduction band (CB) as well as empty states to receive electrons from the valence band (VB). There are several ways of achieving this partial filling. If the IB material is created from the insertion of acceptor-like impurities (Sec. 3) it will be necessary to introduce

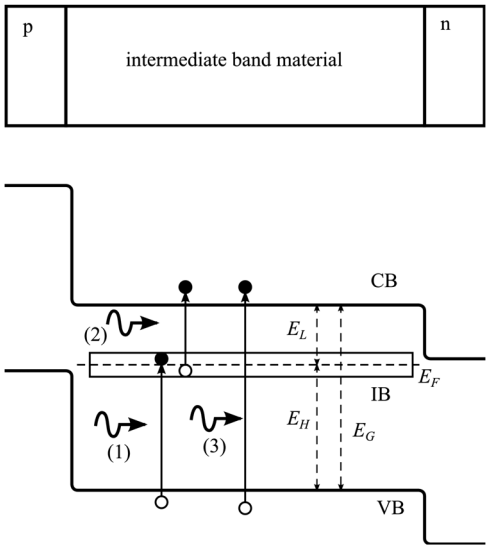


**Fig. 1** Structure of an intermediate band solar cell (IBSC), also showing the simplified bandgap diagram in equilibrium and the photon absorption processes involved.

n-type doping to compensate, and vice versa if the impurities are donor like. If the IB is implemented with quantum dots (QDs) (Sec. 4), with electron confinement in the CB, n-type doping in the barrier, at the approximated dose of one donor per QD, will partially fill the IB created by the QDs.[2] Some works have even suggested that a band that is empty in equilibrium might result partially filled with electrons outside of equilibrium by the intense illumination coming from the use of concentrated light.[3,4] Finally, it might occur that the IB material naturally exhibits this property ($In_2S_3:V$[5] is one example).

Due to its partial filling, the IB allows the absorption of below-bandgap-energy photons in the following way: one below-bandgap-energy photon (photon 1) pumps an electron from the VB to the IB; a second photon (photon 2) pumps an electron from the IB to the CB (these need not be the same electron). The result is the net creation of an electron–hole pair that adds to those directly generated through transitions from the VB to the CB (photon 3). The absorption of below-bandgap-energy photons allows an increased photogenerated current with respect to that of a solar cell with bandgap $E_G$ and no IB. In addition, the output voltage of the cell is still limited to $E_G/e$, with $e$ being the electron charge. For example, if $E_G = 2$ eV, the voltage of the cell is limited to 2 V. It is the potential for achieving high photogenerated current, while preserving the output voltage, that allows a limiting efficiency of 63.2% when operated at maximum concentrated light. From here, we will jump directly into the discussion of the six "easy pieces," which will also allow us to gain insight into the fine details related to the operation of this device. The reader seeking the general reviews of the IBSC fundamentals can consult, e.g., Refs. 6–11, in addition to the ones cited later in this article.

## 2 What happens if the absorption coefficients overlap?

In general, a photon with energy above $E_G$ could be absorbed not only by means of transitions from the VB to the CB but also by means of transitions from the VB to the IB and from the IB to the CB. In this case, the photon energy above the bandgap $E_L$ and $E_H$ is wasted through electron thermalization (Fig. 2). The same applies if a photon with energy above $E_H$ is allowed to be absorbed through transitions from the IB to the CB.

In order to minimize these losses, the absorption coefficients related to each of the three optical transitions should not overlap. The optimum bandgaps, for which the maximum limiting efficiency of 63.2% under maximum concentration has been calculated, are $E_L = 0.71$ eV, $E_H = 1.24$ eV, and $E_G = 1.95$ eV. The reader must be warned that for a practical IBSC, without optimized bandgaps, allowing for some overlap in the absorption coefficients might lead to a higher efficiency than when overlap is not allowed. The reason is that overlapping might produce

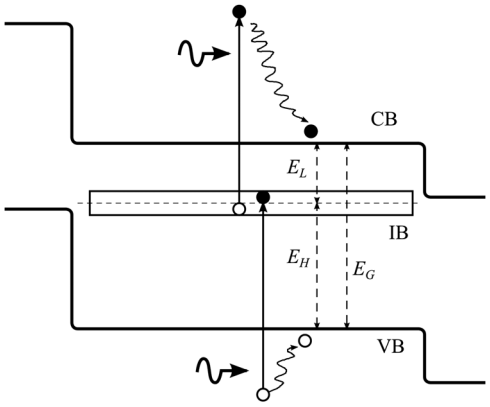


**Fig. 2** Illustration of energy losses by electron thermalization when a photon of energy $E_G$ is allowed to be absorbed through transitions from the VB to the IB or from the IB to the CB.

a better current matching between the VB to IB and the IB to CB transitions that compensates for the above-mentioned thermalization losses. In addition, the negative impact of the absorption coefficient overlap is minimized if, within a given volume of the semiconductor, the strength of one of the competing absorption coefficients is much higher than the others.[12] When the gaps are not optimized, a case by case study would be necessary. Furthermore, if the possibility of using spectrally selected mirrors is accepted, the limiting efficiency is increased.[13]

Another issue is how to avoid the overlap. First, if the strength of the respective absorption coefficients was very different in the energy interval in which they overlap, the same practical effect would be produced as if they did not overlap.[12] Second, cells could be designed in which the emitter absorbs the light with energy above $E_G$, leaving the necessity for the photon absorption selectivity to the IB material itself and to the energy interval that is strictly below the bandgap (Fig. 3). The selectivity at the IB region could be achieved by placing the IB at different energy levels while allowing conduction through it.[14] Lin and Phillips[15] have proposed a way of achieving this by properly engineering QDs.

## 3 What does the Mott's transition have to do with all of this?

To have energy levels inside a semiconductor bandgap is a common feature. In fact, when these energy levels are deep in the semiconductor they are usually called "deep levels," and when they are close to the conduction or VB they are called "shallow levels." The impurities that we call "dopants" produce shallow levels. They are not detrimental for cell performance because, since their energy is located close to the bands, they do not perform as effective nonradiative recombination centers. This follows from Shockley–Read–Hall[16,17] theory, which states that levels closer to the midgap are more harmful as nonradiative recombination centers.

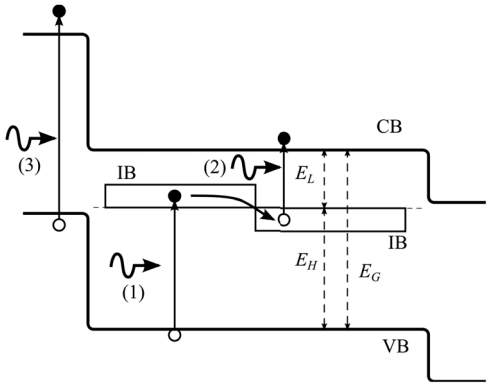


**Fig. 3** Illustration of how to achieve selectivity in photon absorption by splitting the regions where photons are absorbed.

When trying to implement the IBSC in practice, we would like to achieve the energy position that some "deep centers" exhibit (e.g., Ti and Fe in GaAs[18] or $CuGaS_2$[19]) but we do not want the nonradiative recombination they introduce. Would it be possible to keep the location of the energy levels of these impurities while inhibiting the nonradiative recombination they introduce? The solution to this problem was studied in Ref. 20, and the conclusion was that it was possible to inhibit the nonradiative recombination if the wave function of the electrons at the impurities became delocalized. One way of achieving this delocalization is by increasing its density. Mott[21] described the transition from insulating to conducting behavior when the impurity density is increased. However, in Ref. 20, it was postulated for the first time that a sufficiently high impurity density would also produce a transition from nonradiative to radiative recombination, providing a guide to implement an IBSC in practice. In Refs. 22 and 23, experimental evidence supporting this theory was reported by measuring the lifetime of titanium- and sulfur-implanted silicon wafers. Krich et al.[24] have argued against the possibility of an improvement of the lifetime as the impurity concentration increases (so-called lifetime recovery) because, according to their theoretical predictions, the metallic extended states will be localized by phonons during the recombination process. The band anti-crossing mechanism[25] might offer an alternative approach for the IB formation. Under this approach, the IB arises from the insertion into a binary host material of relatively small amounts of a third element, whose orbitals perturb the CB states segregating a band from these states. The appearance of such an IB according to this theory has been reported for ZnTe:O,[26] GaNAsP quaternary alloys,[27] diluted II–VI oxide semiconductors,[28] and GaNAs.[29]

## 4 Does a miniband need to be formed when the IBSC is implemented with QDs?

The use of QDs was proposed as a means to engineer the IBSC. Under this approach, the IB would be formed from the confinement of electrons at the CB offset created between the QD and the barrier material. This approach has usually been sketched as in Fig. 4(a), which suggests the formation of a "miniband." Strictly speaking, the formation of a miniband would take place when the barrier that separates the QDs is so thin that the envelope wave function of the electron at one dot extends through the barrier and reaches the neighboring QD. So, the question here is whether this extension of the wave function into the neighboring dots is necessary at a fundamental level

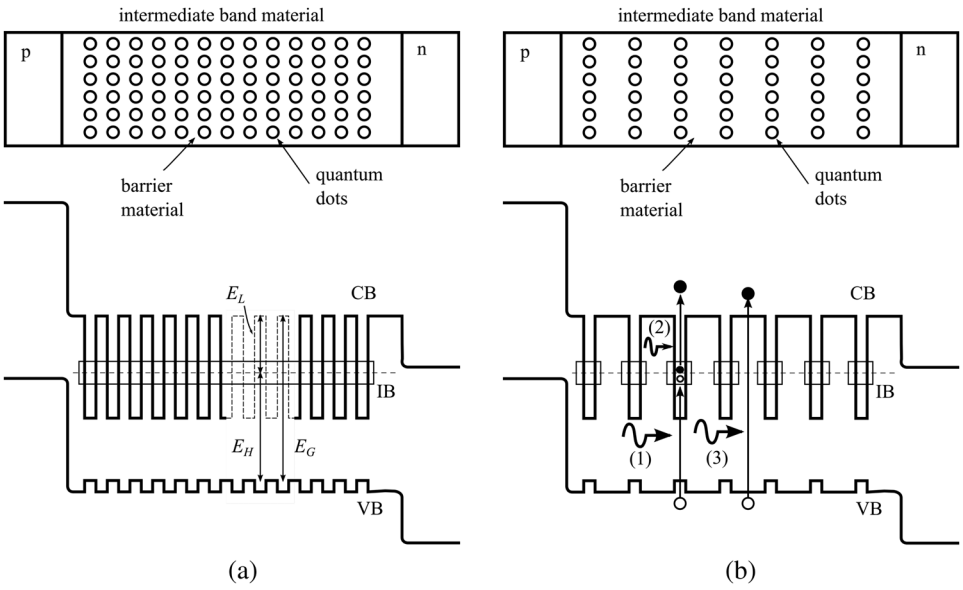


**Fig. 4** (a) Illustration of the quantum dot (QD) approach to the IBSC. (b) The same approach but not necessarily forming a miniband.

for the operation of the IB or not. We think it is not. The formation of a band through the achievement of electron delocalization was necessary when the approach for implementing the IBSC was based on the insertion of impurities as the means to inhibit nonradiative recombination (see Sec. 3). In a QD, the wave function already extends itself over several atoms, and, for the purpose of nonradiative recombination, it could be considered as delocalized. Along this line, nothing to our knowledge prevents the manufacturing of an efficient laser based on a single QD. By the same argument, nothing at the fundamental level prevents the manufacturing of an IBSC on the basis of a single QD (assuming this single QD could provide sufficient light absorption).

Nonetheless, forming a miniband would have practical advantages. An electron–hole pair generated at a QD by the absorption of two below-bandgap-energy photons has a greater chance of being nonradiatively recombined at the barrier as the volume of the barrier increases[30] (if nonradiative recombination mechanisms exist at the barrier). Also, when the absorption coefficient of, e.g., the VB to the IB transition is stronger than that related to the IB to the CB transition, transport through the IB would benefit the performance of the IBSC.[31] Also, proposals based on the creation of a QD-IBSC with different QD sizes, in order to avoid the overlap of absorption coefficients, would demand electron transport through the IB to work well.[15] In any case, achieving a high QD volume density to maximize absorption will result in a scheme in which the dots are so closely packed that the miniband is formed.

From the above discussion, it might look as if the formation of a miniband always has benefits. There is a limit to this: as dots are spaced closer, the energy bandwidth of the miniband increases reducing the effective bandgap $E_L$. This bandgap cannot be reduced to 0 (the limits to IB broadening were studied in Ref. 32). In addition, in most of the experimental devices studied to date (perhaps the ones in Ref. 33 are the only exception), the QDs are located in the space charge region where the existence of a strong electric field tilts the bands. This is due to the reduced thickness of the region containing the QDs and the absence of field damping layers. Under these circumstances, there is one additional effect (illustrated in Fig. 5), which is that, if the barrier is thin, electrons could tunnel directly from the IB to the CB. This would have the side effect of short circuiting the IB with the CB, disabling voltage preservation even if the temperature is decreased. This problem has been extensively studied and experimentally discussed in Ref. 34.

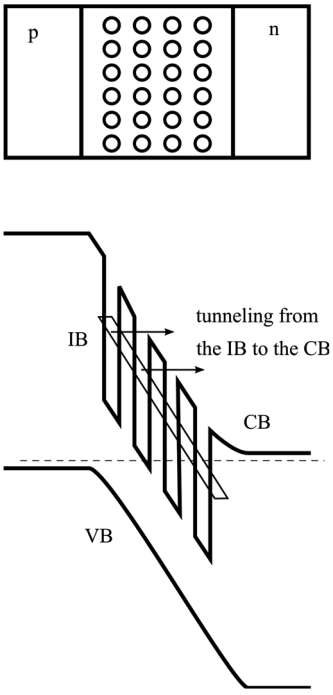


**Fig. 5** Simplified bandgap diagram of a QD IBSC with the QDs in the space charge region, illustrating electron tunneling from the IB to the CB.

## 5 What are the simplest experimental techniques to demonstrate whether an IBSC is working as such or not?

The simplest technique would consist of measuring the efficiency of an IBSC and showing that it is over 45%. Until that moment arrives, we think that: (1) showing that the absorption of two below-bandgap-energy photons can produce one electron–hole pair that can be extracted as photocurrent and (2) that the IB does not limit the open-circuit voltage of the cell, are the two key properties that any IBSC prototype must experimentally verify. It must be emphasized that both properties must concur in the same device.

An experimental setup for verifying the production of photocurrent from the absorption of below-bandgap-energy photons is described in Ref. 33 and reviewed in Ref. 35. It consists of illuminating the cell with a monochromatic beam that has the potential to pump electrons from the VB to the IB but not from the VB to the CB. Then, a second photon beam is introduced with a sufficient energy to pump electrons from the IB to the CB but not from the VB to the IB. If the absorption of two below-bandgap-energy photons is taking place, this second beam should produce an increment in photocurrent. In existing prototypes, the photon pumping of electrons from to the IB to the CB is competing with thermal escape between these two bands. Temperature must usually be decreased in the experiments so that the two-photon effect can be measured. Performing this measurement also allows identification of the energy absorption threshold and, therefore, the location of the IB inside the bandgap. The absorption of two below-bandgap-energy photons to produce one electron–hole pair has been experimentally demonstrated in IBSCs based on QDs,[33,36–38] in ZnTe:O[39] and in GaNAs[40] (in some cases, without the need of decreasing the temperature).

In order to verify that the IB does not limit the output voltage, the easiest experiment is perhaps to demonstrate that the cell is capable of producing an open-circuit voltage that (multiplied by the electron charge) is higher than the photon absorption threshold. For that, the cell can be illuminated with concentrated light[41] or with a laser beam.[42] Temperature also has to be decreased to avoid the competition of thermal escape. Voltages not limited by the IB have been measured in QD-IBSCs.[41,42]

## 6 What are the problems for each of the main practical approaches that exist today?

As mentioned in the previous sections, there are two main approaches that have been experimentally investigated to implement the IBSC: the QD and the impurity approach.

In the QD approach, both the principle of absorption of two below-bandgap-energy photons and the voltage preservation have been demonstrated. However, the absorption of below bandgap light has been too weak producing only small increments in photocurrent and it has not been until recently that cells have been manufactured in which this increment has not been accompanied by an excessive voltage drop at one sun and room temperature.[43] Studies are underway in order to gain insight about the impact that size[44] and symmetry[45,46] have on the strength of the light absorption by the dots. On the other hand, the systems that have been used are based on InAs/GaAs. Although this system can lead to efficiencies above that of GaAs under concentrated light, the gap of the GaAs is still far from the optimum predicted for an ideal IBSC (around 2 eV). Besides, from a practical point, the growth of the QDs has been based on the Stranski–Krastanov method,[47] which demands that some strain exists between the barrier and the QD material so that the dots can nucleate. When the barriers are too thin, strain can accumulate to the emitter of the cell degrading the efficiency of the cell.[48] The use of strain compensation[43,49] or droplet epitaxy[50–52] techniques can avoid this accumulation and increase the number of layers that can be grown without defects.

Regarding the impurity approach, the main challenge is perhaps the difficulty in finding an impurity leading to an IB at the appropriate energy location inside the semiconductor bandgap that, at the same time, has a sufficiently high solubility in the semiconductor as to be incorporated at high density without forming clusters or inducing the appearance of third undesired defects. Nonequilibrium techniques, such as the use of ionic implantation followed by rapid thermal laser annealing have been reported as being successful when attempting to create an

IB from the insertion of Ti[53] and S[23] in silicon. The use of highly mismatched alloys, where the IB emerges from the band-anti-crossing mechanism mentioned in the previous sections ($ZnTe:O$[39] and GaNAs[40]), might also be a successful approach.

## 7 What would the best system be, if any?

This is the most difficult piece. As explained in the previous section, each approach has its own advantages and drawbacks. It is not possible for us to choose a winner. Instead, with our present knowledge, we can provide directions for possible future works where perhaps the winner can be found.

First, as mentioned, any of the approaches for which some experimental result exists (QDs, impurities…) exhibit poor absorption for below-bandgap-energy photons. Increasing light absorption is a problem that is not exclusive to IBSCs. Absorption of light in thin film solar cells, e.g., is an area of increased interest in photovoltaics since absorbing the same amount of light in less volume will improve the efficiency of the cells (by reducing nonradiative recombination) while reducing the cost by using less of materials. Several approaches are being followed in this respect that explore the possibility of using plasmon resonance[54–56] or diffraction grids.[57] Success in any of the strategies that are being followed in this respect might positively impact the performance of the IBSCs that have already been developed.

On the other hand, the QD approach demands that the energy of the bandgap $E_L$ is increased in order to minimize the impact of thermal escape at room temperature.[58] Besides, while using GaAs barriers, the total bandgap of the cell (1.4 eV) still has room for improvement. Substituting[59,60] the GaAs by AlGaAs or InGaP barriers would assist in moving simultaneously toward the achievement of both targets. In order to increase the absorption of light by the dots, their density and number of layers will need to be increased. In this respect, the use of high index substrates[38,61] (such as 311B) might allow the areal dot density to approach the range $10^{12}$ $cm^{-2}$. Other systems, different from III to Vs and in which the dot nucleation is based on the different crystallization system between dot and barrier materials, have also been proposed[62] as an alternative to the strain compensating technique used when growing in the Stranski–Krastanov mode.

Finally, there are several systems and materials that have been theoretically proposed but have not been taken into practice as complete solar cells. Some examples are $InS_3:V$[5] (synthesized in powder form, the absorption coefficient of the experimental material agrees with theoretical predictions[63]), $MgIn_2S_4:Ti$,[64] $In_{1-x}Ga_xN:Mn$,[65] $SZn:Cr$, $TeZn:Cr$[66] and some molecular approaches,[67] organic approaches,[68] and colloidal QDs together with metal nanoparticles.[69] At present, there is such an explosive amount of IBSC candidates that it might well happen that the final winner is still hidden among them.

## 8 Summary

Several questions related to research in IBSCs have been addressed in this article and answered to the extent of our present understanding. The absorption coefficients involved in the operation of an IBSC should not overlap to allow a fully optimized device to achieve its limiting efficiency. However, it is possible that nonoptimized devices (because, e.g., the IB is not at the optimum position) perform better if the absorption coefficients overlap, due to a better current matching between the CB and the VB through the IB. The "Mott's transition" serves as a reference to estimate the impurity concentration that is required to inhibit nonradiative recombination through the IB due to the delocalization of the electron wave function at the IB. Nevertheless, other mechanisms also leading to wave function delocalization could also produce the same effect. A miniband does not need to be formed when implementing the IBSC with QDs, although its formation might boost the performance of the devices. From an experimental point of view, an IBSC candidate should verify that the absorption of two below-bandgap-energy photons produces one net electron–hole pair and that the IB does not limit the output voltage of the cell. The first can be verified through quantum efficiency measurements and the second through light concentration measurements. Both the QD and the impurity approach to the IBSC present its own problems. For example, the QD approach is affected by the weak sub-bandgap

absorption and the impurity approach is affected by the difficulty of finding impurities that can be incorporated at high densities without forming clusters. There is not yet a clear winner and, in fact, it might still be hidden among the many systems that have been proposed but not yet studied. (The title of this article is a small tribute to the work by R.P. Feynman, "Six not so easy pieces."[70])

## Acknowledgments

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## References

1. A. Luque and A. Martí, "Increasing the efficiency of ideal solar cells by photon induced transitions at intermediate levels," *Phys. Rev. Lett.* **78**(26), 5014–5017 (1997), http://dx.doi.org/10.1103/PhysRevLett.78.5014.
2. A. Martí, L. Cuadra, and A. Luque, "Partial filling of a quantum dot intermediate band for solar cells," *IEEE Trans. Electron Dev.* **48**(10), 2394–2399 (2001), http://dx.doi.org/10.1109/16.954482.
3. R. Strandberg and T. W. Reenaas, "Photofilling of intermediate bands," *J. Appl. Phys.* **105**(12), 124512 (2009), http://dx.doi.org/10.1063/1.3153141.
4. A. Luque and A. Marti, "On the partial filling of the intermediate band in IB solar cells," *IEEE Trans. Electron Dev.* **57**(6), 1201–1207 (2010), http://dx.doi.org/10.1109/TED.2010.2045681.
5. R. Lucena et al., "Synthesis and spectral properties of nanocrystalline V-substituted In2S3, a novel material for more efficient use of solar radiation," *Chem. Mater.* **20**(16), 5125–5151 (2008), http://dx.doi.org/10.1021/cm801128b.
6. A. Martí, L. Cuadra, and A. Luque, *Intermediate Band Solar Cells*, Institute of Physics Publishing, Bristol (2003).
7. A. Martí and A. Luque, *Fundamentals of Intermediate Band Solar Cells*, Springer Series in Optical Sciences, Berlin (2012).
8. A. Martí, C. R. Stanley, and A. Luque, *Intermediate Band Solar Cells (IBSC) Using Nanotechnolgy*, Vol. 17, Elsevier, Amsterdam (2006).
9. E. Antolín, A. Martí, and Luque A., *High Efficiency Intermediate Band Solar Cells Implemented with Quantum Dots*, CRC, Boca Raton (2010).
10. P. G. Linares et al., *Intermediate Band Solar Cells: Modeling and Simulation*, Hershey, Pennsylvania (2012).
11. A. Luque and A. Martí, "The intermediate band solar cell: progress toward the realization of an attractive concept," *Adv. Mater.* **22**(2), 160–174 (2010), http://dx.doi.org/10.1002/adma.v22:2.
12. L. Cuadra, A. Martí, and A. Luque, "Influence of the overlap between the absorption coefficients on the efficiency of the intermediate band solar cell," *IEEE Trans. Electron Dev.* **51**(6), 1002–1007 (2004), http://dx.doi.org/10.1109/TED.2004.828161.
13. R. Strandberg and T. W. Reenaas, "Limiting efficiency of intermediate band solar cells with spectrally selective reflectors," *Appl. Phys. Lett.* **97**(3), 031910 (2010), http://dx.doi.org/10.1063/1.3466269.
14. M. Yoshida et al., "Photon ratchet intermediate band solar cells," *Appl. Phys. Lett.* **100**(26), 263902 (2012), http://dx.doi.org/10.1063/1.4731277.
15. A. Lin and J. Phillips, "Decoupling spectral overlap of intermediate band solar cells using low-high state filling," in *38th IEEE Photovoltaic Specialists Conference (PVSC)*, pp. 000073–000077, IEEE, New York (2012).
16. W. Shockley and W. T. Read, "Statistics of the recombination of holes and electrons," *Phys. Rev.* **87**(5), 835–842 (1952), http://dx.doi.org/10.1103/PhysRev.87.835.

17. R. N. Hall, "Electron-hole recombination in germanium," *Phys. Rev.* **87**(2), 387 (1952), http://dx.doi.org/10.1103/PhysRev.87.387.
18. A. Marti et al., "IBPOWER: intermediate band materials and solar cells for photovoltaics with high efficiency and reduced cost," in *Proc. 34th IEEE PVSC*, IEEE, New York (2009).
19. A. Martí, D. F. Marrón, and A. Luque, "Evaluation of the efficiency potential of intermediate band solar cells based on thin-film chalcopyrite materials," *J. Appl. Phys.* **103**(7), 073706 (2008), http://dx.doi.org/10.1063/1.2901213.
20. A. Luque et al., "Intermediate bands versus levels in non-radiative recombination," *Physica B* **382**(1–2), 320–327 (2006), http://dx.doi.org/10.1016/j.physb.2006.03.006.
21. N. F. Mott, "Metal-insulator transition," *Rev. Mod. Phys.* **40**(4), 677–683 (1968), http://dx.doi.org/10.1103/RevModPhys.40.677.
22. E. Antolin et al., "Lifetime recovery in ultrahighly titanium-doped silicon for the implementation of an intermediate band material," *Appl. Phys. Lett.* **94**(4), 042115 (2009), http://dx.doi.org/10.1063/1.3077202.
23. P. D. Persans et al., "Photocarrier lifetime and transport in silicon supersaturated with sulfur," *Appl. Phys. Lett.* **101**(11), 111105 (2012), http://dx.doi.org/10.1063/1.4746752.
24. J. J. Krich, B. I. Halperin, and A. Aspuru-Guzik, "Nonradiative lifetimes in intermediate band photovoltaics—absence of lifetime recovery," *J. Appl. Phys.* **112**(1), 013707 (2012), http://dx.doi.org/10.1063/1.4732085.
25. W. Shan et al., "Band anticrossing in GaInNAs alloys," *Phys. Rev. Lett.* **82**(6), 1221–1224 (1999), http://dx.doi.org/10.1103/PhysRevLett.82.1221.
26. T. Tanaka et al., "Demonstration of ZnTe(1–x)O(x) intermediate band solar cell," *Jap. J. Appl. Phys.* **50**(8), 082304 (2011), http://dx.doi.org/10.1143/JJAP.50.082304.
27. K. M. Yu et al., "Multiband GaNAsP quaternary alloys," *Appl. Phys. Lett.* **88**(9), 092110 (2006), http://dx.doi.org/10.1063/1.2181627.
28. K. M. Yu et al., "Diluted II–VI oxide semiconductors with multiple band gaps," *Phys. Rev. Lett.* **91**(24), 246403 (2003), http://dx.doi.org/10.1103/PhysRevLett.91.246403.
29. N. Lopez et al., "Engineering the electronic band structure for multiband solar cells," *Phys. Rev. Lett.* **106**(2), 028701 (2011), http://dx.doi.org/10.1103/PhysRevLett.106.028701.
30. A. Martí, L. Cuadra, and A. Luque, "Design constraints of the quantum-dot intermediate band solar cell," *Physica E* **14**(1–2), 150–157 (2002), http://dx.doi.org/10.1016/S1386-9477(02)00368-5.
31. A. Martí, L. Cuadra, and A. Luque, "Quasi drift-diffusion model for the quantum dot intermediate band solar cell," *IEEE Trans. Electron Dev.* **49**(9), 1632–1639 (2002), http://dx.doi.org/10.1109/TED.2002.802642.
32. A. Martí, L. Cuadra, and A. Luque, *Quantum Dot Analysis of the Space Charge Region of Intermediate Band Solar Cell*, The Electrochemical Society, Pennington (2001).
33. A. Martí et al., "Production of photocurrent due to intermediate-to-conduction-band transitions: a demonstration of a key operating principle of the intermediate-band solar cell," *Phys. Rev. Lett.* **97**(24), 247701 (2006), http://dx.doi.org/10.1103/PhysRevLett.97.247701.
34. E. Antolin et al., "Reducing carrier escape in the InAs/GaAs quantum dot intermediate band solar cell," *J. Appl. Phys.* **108**(6), 064513 (2010), http://dx.doi.org/10.1063/1.3468520.
35. A. Marti et al., "Understanding experimental characterization of intermediate band solar cells," *J. Mater. Chem.* **22**(43), 22832–22839 (2012).http://dx.doi.org/10.1039/C2JM33757F
36. Y. Okada et al., "Increase in photocurrent by optical transitions via intermediate quantum states in direct-doped InAs/GaNAs strain-compensated quantum dot solar cell," *J. Appl. Phys.* **109**(2), 024301 (2011), http://dx.doi.org/10.1063/1.3533423.
37. E. Antolín et al., "Demonstration and analysis of the photocurrent produced by absorption of two sub-bandgap photons in a quantum dot intermediate band solar cell," in *Proc. 23th European Photovoltaic Solar Energy Conference (Valencia)*, pp. 5–10, WIP Renewable Energies, Munich (2008).
38. Y. Shoji et al., "Effect of spacer layer thickness on multi-stacked InGaAs quantum dots grown on GaAs (311)B substrate for application to intermediate band solar cells," *J. Appl. Phys.* **111**(7), 074305 (2012), http://dx.doi.org/10.1063/1.3699215.

39. W. Wang, A. S. Lin, and J. D. Phillips, "Intermediate-band photovoltaic solar cell based on ZnTe:O," *Appl. Phys. Lett.* **95**(1), 011103 (2009), http://dx.doi.org/10.1063/1.3166863.
40. N. Ahsan et al., "Two-photon excitation in an intermediate band solar cell structure," *Appl. Phys. Lett.* **100**(17), 172111–172114 (2012), http://dx.doi.org/10.1063/1.4709405.
41. P. G. Linares et al., "Voltage recovery in intermediate band solar cells," *Solar Energy Mater. Solar Cells* **98**(0), 240–244 (2012), http://dx.doi.org/10.1016/j.solmat.2011.11.015.
42. E. Antolin et al., "Advances in quantum dot intermediate band solar cells," in *35th IEEE Photovoltaic Specialists Conference (PVSC)*, pp. 000065–000070, IEEE, New York (2010).
43. C. G. Bailey et al., "Open-circuit voltage improvement of InAs/GaAs quantum-dot solar cells using reduced InAs coverage," *IEEE J. Photovoltaics* **2**(3), 269–275 (2012), http://dx.doi.org/10.1109/JPHOTOV.2012.2189047.
44. A. Mellor et al., "The influence of quantum dot size on the sub-bandgap intraband photocurrent in intermediate band solar cells," *Appl. Phys. Lett.* **101**(13), 133909 (2012), http://dx.doi.org/10.1063/1.4755782.
45. A. Luque et al., "Symmetry considerations in the empirical k.p Hamiltonian for the study of intermediate band solar cells," *Solar Energy Mater. Solar Cells* **103**(0), 171–183 (2012), http://dx.doi.org/10.1016/j.solmat.2012.04.015.
46. A. Luque et al., "Virtual-bound, filamentary and layered states in a box-shaped quantum dot of square potential form the exact solution of the effective mass Schrödinger equation," *Physica B* **413**, 73–81 (2013), http://dx.doi.org/10.1016/j.physb.2012.12.047.
47. M. Sugawara, *Self-assembled InGaAs/GaAs Quantum Dots*, Academic Press, Amsterdam (1999).
48. A. Marti et al., "Emitter degradation in quantum dot intermediate band solar cells," *Appl. Phys. Lett.* **90**(23), 233510 (2007), http://dx.doi.org/10.1063/1.2747195.
49. V. Popescu et al., "Theoretical and experimental examination of the intermediate-band concept for strain-balanced (In,Ga)As/Ga(As,P) quantum dot solar cells," *Phys. Rev. B* **78**(20), 205321 (2008), http://dx.doi.org/10.1103/PhysRevB.78.205321.
50. J. Wu et al., "Intermediate-band material based on GaAs quantum rings for solar cells," *Appl. Phys. Lett.* **95**(7), 071908 (2009), http://dx.doi.org/10.1063/1.3211971.
51. J. Wu et al., "Intersublevel infrared photodetector with strain-free GaAs quantum dot pairs grown by high-temperature droplet epitaxy," *Nano Lett.* **10**(4), 1512–1516 (2010), http://dx.doi.org/10.1021/nl100217k.
52. J. Wu et al., "Strain-free ring-shaped nanostructures by droplet epitaxy for photovoltaic application," *Appl. Phys. Lett.* **101**(4), 043904 (2012), http://dx.doi.org/10.1063/1.4738996.
53. H. Castan et al., "Experimental verification of intermediate band formation on titanium-implanted silicon," *J. Appl. Phys.* **113**(2), 024104 (2013), http://dx.doi.org/10.1063/1.4774241.
54. H. A. Atwater and A. Polman, "Plasmonics for improved photovoltaic devices," *Nat. Mater.* **9**(3), 205–213 (2010), http://dx.doi.org/10.1038/nmat2629.
55. A. Luque et al., "Light absorption in the near field around surface plasmon polaritons," *J. Appl. Phys.* **104**(11), 113118 (2008), http://dx.doi.org/10.1063/1.3014035.
56. M. J. Mendes et al., "Plasmonic light enhancement in the near-field of metallic nanospheroids for application in intermediate band solar cells," *Appl. Phys. Lett.* **95**(7), 071105 (2009), http://dx.doi.org/10.1063/1.3205470.
57. A. Mellor et al., "A numerical study of Bi-periodic binary diffraction gratings for solar cell applications," *Solar Energy Mater. Solar Cells* **95**(12), 3527–3535 (2011), http://dx.doi.org/10.1016/j.solmat.2011.08.017.
58. A. Luque et al., "Radiative thermal escape in intermediate band solar cells," *AIP Adv.* **1**(2), 022125 (2011), http://dx.doi.org/10.1063/1.3597326.
59. P. G. Linares et al., "III–V compound semiconductor screening for implementing quantum dot intermediate band solar cells," *J. Appl. Phys.* **109**(1), 014313 (2011), http://dx.doi.org/10.1063/1.3527912.
60. I. Ramiro et al., "InAs/AlGaAs quantum dot intermediate band solar cells with enlarged sub-bandgaps," in *Proc. 38th IEEE Photovoltaic Specialists Conference*, IEEE, New York (2012).

61. K. Akahane et al., "Fabrication of ultra-high density InAs-stacked quantum dots by strain-controlled growth on InP(311)B substrate," *J. Cryst. Growth* **245**(1–2), 31–36 (2002), http://dx.doi.org/10.1016/S0022-0248(02)01701-3.
62. E. Antolín, A. Martí, and A. Luque, "The lead salt quantum dot intermediate band solar cell," in *Proc. 37th IEEE PVSC*, IEEE, New York (2011).
63. P. Palacios et al., "Transition-metal-substituted indium thiospinels as novel intermediate-band materials: prediction and understanding of their electronic properties," *Phys. Rev. Lett.* **101**(4), 046403 (2008), http://dx.doi.org/10.1103/PhysRevLett.101.046403.
64. I. Aguilera, P. Palacios, and P. Wahnon, "Understanding Ti intermediate-band formation in partially inverse thiospinel MgIn2S4 through many-body approaches," *Phys. Rev. B* **84**(11), 6 (2011), http://dx.doi.org/10.1103/PhysRevB.84.115106.
65. A. Martí et al., "Potential of Mn doped In1-xGaxN for implementing intermediate band solar cells," *Solar Energy Mater. Solar Cells* **93**(5), 641–644 (2009), http://dx.doi.org/10.1016/j.solmat.2008.12.031.
66. C. Tablero, "Survey of intermediate band materials based on ZnS and ZnTe semiconductors," *Solar Energy Mater. Solar Cells* **90**(5), 588–596 (2006), http://dx.doi.org/10.1016/j.solmat.2005.04.036.
67. N. J. Ekins-Daukes and T. W. Schmidt, "A molecular approach to the intermediate band solar cell: the symmetric case," *Appl. Phys. Lett.* **93**(6), 063507 (2008), http://dx.doi.org/10.1063/1.2970157.
68. S. R. Forrest, "Intermediate-band photosensitive device with quantum dots having tunneling barrier embedded in organic matrix," US patent 7,414,294 B2 (2008).
69. M. Mendes et al., "Intermediate band solar cell having solution processed colloidal quantum dots," US patent request n0 61/547,312 (2011).
70. R. P. Feynman, *Six Not so Easy Pieces*, Penguin Books, London (1999).