

Tandem Solar Cells Using Ternary and Quaternary Compound Semiconductors

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Abstract

Tandem architectures have become of interest due to the quest to realise greater efficiency in solar photovoltaic technologies as a way to overcome the inherent shortcomings of single-junction devices. In ternary and quaternary compound semiconductors, such as Cu(In,Ga)Se₂ (CIGS), Cu₂ZnSnS₄ (CZTS), Cu₂ZnSn(S,Se)₄ (CZTSSe), and Cu(In,Ga)(S,Se)₂ (CIGSeS), a range of available band gaps, coupled with high absorption coefficients, and scalability to thin-film technologies provides high potential in the field. The basic principles of tandem solar cell operation, the importance of ternary and quaternary absorbers, and plan to band-gap engineer cells to make the most of spectral sculpting and current density, is addressed in this paper.

Recent improvements are record single-junction efficiencies of more than 23% of CIGS and of the order of 13% of CZTSSe, and simulated tandem efficiencies of almost 30% with finely tuned band-gaps. There is still difficulty in this reversing open-circuit voltage deficits, defect states, secondary phase formation and element scarcity of elements like indium and gallium. Alternatives such as kesterite compounds that are sustainable are promising but performance falls short. The future prognosis is to have a hybrid tandem of perovskite with kesterite or chalcopyrite absorbers, the application of which provides the possibility of reaching efficiencies of over 35.

Altogether, the development of tandem solar cell with ternary and quaternary semiconductors is a radical change in the history of photovoltaics as it stands as efficiency, sustainability and scalability to the needs of the global renewable energy usage.

1. Introduction

Renewable energy technologies have become the focus of scientific and industrial attention in relation to meeting the increasing global energy demand and the necessity to reduce climate change. Solar photovoltaics (PV) are one of the most promising, as well as the fastest developing, energy sources because they are scalable, modular, and costs are expected to be decreasing (Green et al., 2023). Traditional single-junction solar cells however have a theoretical efficiency limit referred to as the Shockley-Queisser (SQ) limit, that limits

the optimal conversion efficiency to approximately 33 percent when in a typical illumination environment (Shockley and Queisser, 1961). This is disadvantageous since a common semiconductor material cannot effectively absorb all the sun rays. The energy of high-energy photons is dissipated as heat and the energy of low-energy photons penetrates without being absorbed.

To circumvent this issue multi-junction or tandem solar cells have appeared as a good

direction to take. They are made up of deposits of several semiconductors that exhibit varying band gaps, each being bound to absorbing a given spectral slice of the solar spectrum. This design will greatly decrease thermalization/transmission losses, and theoretically has efficiencies of over 40 percent (Yang et al., 2020). This type of performance through enhancement mainstreams tandem structures as a plausible pathway to the next generation PV systems, which are able to satisfy ambitious energy requirements using less materials and space.

In the given paradigm, tunable band gaps, the high absorption coefficients, as well as the possibility of low-cost, scalable manufacturing has been garnering significant interest in the use of compound semiconductors, especially in the ternary and quaternary chalcogenides (Polizzotti et al., 2013; Mitzi et al., 2011). Two material classes have dominated this research, which include copper indium gallium selenide (CIGS), and copper zinc tin sulfide/selenide (CZTSSe). CIGS is a ternary alloy system that has proven record efficiencies of over 23% in single-junction systems and can tune over a wide range by simply changing the gallium to indium ratio (Jackson et al., 2016). CZTSSe however is an earth-abundant and non-toxic element, which makes it a viable alternative. Its direct band together with high absorption coefficient of about 1.0-1.5 eV makes it especially than the ideal material to be used in tandem though efficiency is restricted due to various other factors such as defects and second phase formation (Yang et al., 2022).

The ternary and quaternary compounds integrated in tandem structures have their own merits in giving exclusive chances of band-gap engineering, which is of critical concerns in the optimization of energy singular conversion.

Using the sulfur-to-selenium counter where the proportion of sulfur versus selenium was adjusted or using gallium-to-indium, scientists could precisely modulate the band gaps which would yield current matching between sub-cells and forms a condition of high-efficiency tandem gadgets (Chen et al., 2020). In addition, the progress of deposition techniques, such as sputtering, solution-based techniques, and atomic layer deposition, have enhanced the qualities of materials, providing new developmental opportunities of scalability in manufacturing (Kumar et al., 2021).

Although these improvements have been made, there are still issues of commercial viability in creating tandem equipment using compound semiconductors. Endemic deficit in *voc*, non-radiative recombination and long-term stability in stressed situations during operation are inexorable obstacles (Todorov et al., 2013). The interface engineering, the passivation of the defects, and the design of the robust tunnel junctions are also an active field of research in order to address these problems. However, the recent advances of both experimentation and theoretical studies point out the great prospect of ternary and quaternary semiconductors as facilitating materials of thin-film multicolor solar cells.

At this point, the present paper discusses the application of compound semiconductor materials including CIGS and CZTSSe in tandem configuration where bandgap engineering is critically important in maximizing energy conversion. This work places tandem solar cells as a revolution in the world of sustainable and high-efficiency photovoltaics by studying its material characteristics, its design approaches as well as its recent technological achievements.

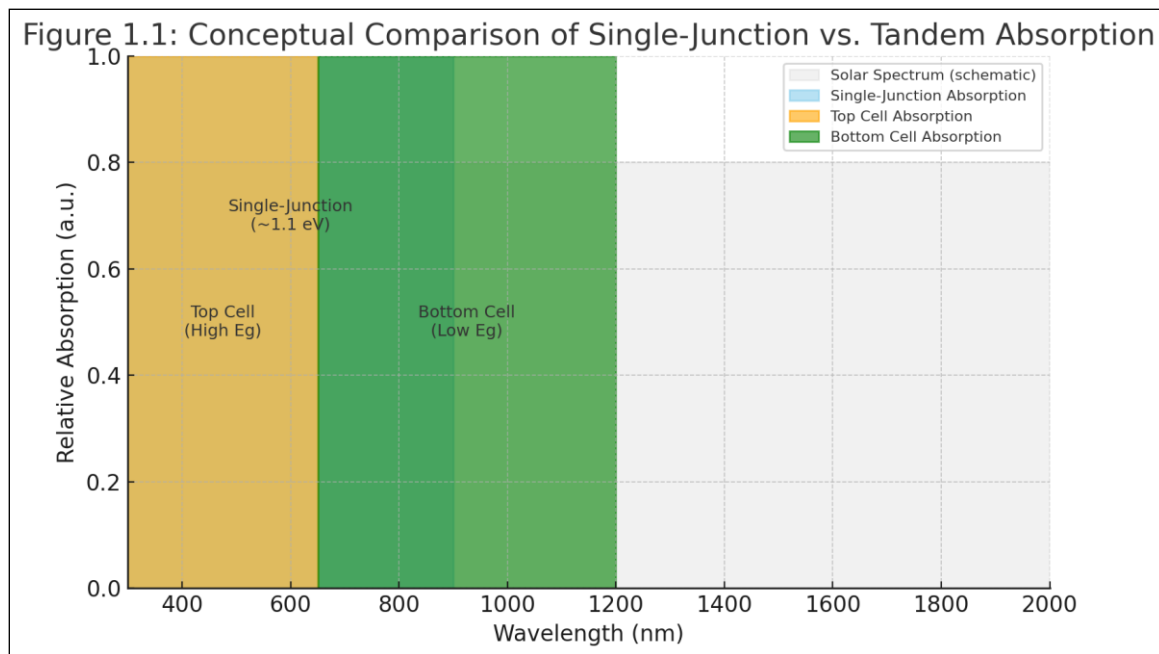


Figure 1.1: *Conceptual Comparison of Single-Junction vs. Tandem Absorption*

2. Basics of Tandem Solar Cells

The rationale behind tandem solar cells is simply to exceed the efficiency limit of monolithic single-junction devices. As mentioned above, the efficiency of an individual absorber made out of semiconductor is limited by what is known as the Shockley-Queisser (SQ) limit and it is estimated to reach up to 33 percent in cold test conditions (Shockley and Queisser, 1961). This is limited by two inherent energy losses: 1) thermalization loss, high-energy photons lose extra energy as heat, and 2) transmission loss, in which low-energy photons lower than the energy of the bandgap travel unabsorbed. These losses are overcome using tandem or multi-junction designs, which stack semiconductors of varying bandgaps, with any given semiconductor absorbing a different part of the solar spectrum (De Wolf et al., 2019).

Parallel vs. Series Concordances

Tandem solar cells can be designed in two formats; in monolithic (series-connected) and

in mechanically stacked (parallel-connected) formats.

- i. Serial connected tandem cells need tuning of the band-gaps to obtain sub-cell matching current. The minimum performing sub-cell limits the overall photocurrent, however, the output voltage is junction additive. Tunnel junctions Monolithic devices Monolithic integration often requires device layout set around tunnel junctions and requires stored lattice and band alignment (Geisz et al., 2020).
- ii. Parallel-connected tandems have sub-cells with parallel coupling so that there are no current matching requirements. Nonetheless, this design is less popular because there is increased complexity in designing devices, and couple optical losses.

Selection of Material and Band-Gap Engineering

The choice of the absorber material of tandem architectures plays a crucial role in the

maximization of performances of the devices. The optimal design would be a wide-band-gap top cell (1.6-1.8 eV) to absorb high-energy photons, and a narrow-band-gap bottom cell (1.0-1.2 eV) to absorb the lower-energy part of the spectrum (Almansouri et al., 2018). Compound semiconductors: Cadmium-zinc-tehtride (CdZnTe), cadmium- calcium-zinc-tehtride (CdCaZnTe), and quaternary variants are promising materials with a variable controllable band gap and high absorption coefficient. Key to designing an efficient tandem structure is band-gap engineering, which eliminates bandgaps by compositional tuning (e.g. Ga/In or S/Se ratio).

Tunnel Junctions and Recombination Layers

Electrical connection of sub-cells is done with the help of tunnel junctions in series-connected tandem devices without optical transparency affecting the result. The layers adopt efficient

carrier transportation in between layers; these layers will not add significant optical or electrical losses (King et al., 2012). The material compatibility, doping levels and defect passivation are important to help minimize the possibility of the tunnel junction limiting the efficiency of a device.

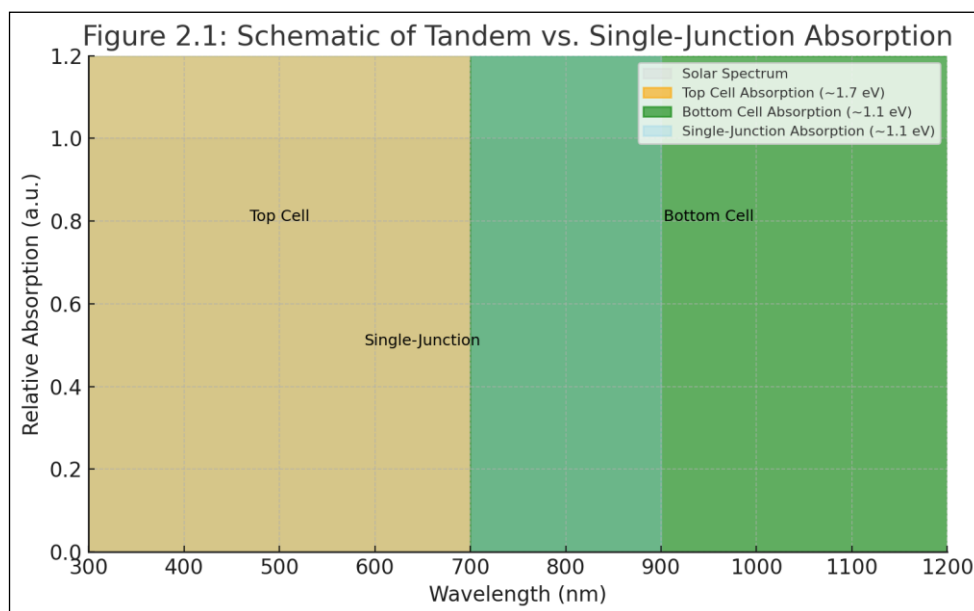
Efficiency Potential

Multiple computations have estimated that a dual-junction tandem can in principle reach efficiencies of approximately 42 percent, and triple-junction cells can theoretically reach some combination of greater than 50 percent when in concentrated sunlight (Green et al., 2023). Only real-world performance falls short of these values because of non-idealities like defect-induced recombination, parasitic absorption and thermal instabilities. However, the tandem approach is one of the most promising next-generation photovoltaics approaches.

Table 2.1: Comparison of Single-Junction vs. Tandem Solar Cells

Feature	Single-Junction Solar Cell	Tandem Solar Cell (Dual-Junction)
Theoretical Efficiency Limit	~33% (Shockley–Queisser)	~42% (dual) / ~50%+ (triple)
Spectrum Utilization	Limited (thermalization, losses)	Broad, covering multiple energy ranges
Device Structure	Single absorber layer	Stacked absorbers with tunnel junctions
Current Matching Requirement	Not applicable	Required for series-connected tandems
Material Choices	Si, GaAs, CdTe, CIGS	CIGS, CZTS, CZTSSe, Perovskite hybrids
Commercial Status	Mature, widely deployed	Emerging, experimental to pilot scale

Figure 2.1:



Schematic of Tandem vs. Single-Junction Absorption

3. Tertiary Compound Semiconductors

Third generation compound semiconductors like $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) and $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) have been proposed as prospective thin-film photovoltaics absorber and tandem solar cell designs. Flexibility in band-gap engineering and high light absorption characteristics in these materials should be combined with scalability to large areas through deposition methods and make them well-submitted candidates to outperform next-generation devices (Polizzotti et al., 2013).

$\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS)

One of the most investigated ternary semiconductors is CIGS with the band gap that can be tuned between 1.0 and 1.7 eV depending on the Ga/(In+Ga) ratio (Jackson et al., 2016). Such flexibility gives CIGS both the features of a top and bottom cell in tandem layouts. Besides the large absorption coefficient ($>10^5 \text{ cm}^{-1}$), CIGS is characterized by long carrier lifetimes and high defect tolerance, allowing it to achieve above-record-single-junction efficiencies of over 23%. It is

also compatible with flexible substrates, which also ensures that it was applicable in lightweight and portable PV systems. Nonetheless, the combination of the limited sources of these materials (indium and gallium) and the need to be produced on a large scale presents a challenge to sustainability and cost of deployment (Green et al., 2023).

$\text{Cu}_2\text{ZnSnS}_4$ (CZTS)

CZTS is a non-toxic outdoor kesterite-structured semiconductor created with earth-abundant elements, and hence an environmentally friendly replacement to CIGS (Mitzi et al., 2011). It possesses a direct band gap of almost exactly 1.5 eV, almost precisely what one requires to convert solar energy to forms accessible to electronics. CZTS has absorption coefficient of high value (approximately 10^4 cm^{-1}) and due to this capacity, can absorb sunlight in thin layers. Although it has these benefits, its devices still have a lower performance, and the record efficiencies are at about 12-13% (Yang et al.,

2022). The reasons that contribute to efficiency gap include antisite defect, cation disorder and secondary phase formation (e.g., ZnS, SnS) resulting in open-circuit voltage deficiency and losses caused by recombination (Todorov et al., 2013).

Role Architectures Tandem Role Architectures Role Role Elementaries

CIGS is commonly used in tandem solar cells, with a wide-band-gap top cell (typically of the order of 1.7 eV) with lower band-gap materials such as silicon or CZTSSe matched to current. Conversely, CZTS has the capability of operating as a bottom cell because it has a desirable band gap (~1.012 eV alloyed with selenium), which centers on complementing top-cell wide band-gap absorbers (Chen et al., 2020). It is the combination of these semiconductors which, therefore, makes it

possible to implement the utilization of broad spectrum at personally friendly material portfolio.

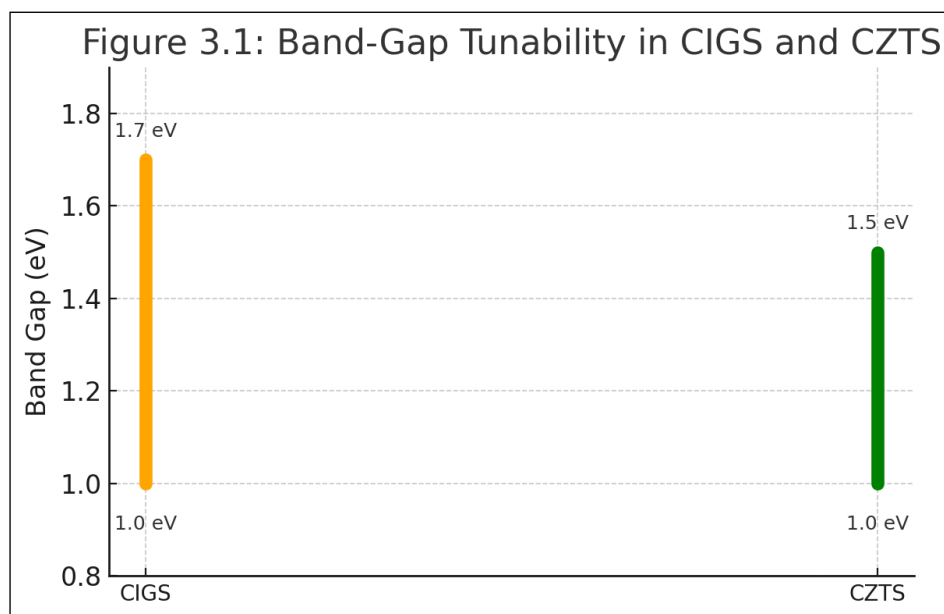
Difficulties and Prospects

Despite CIGS being a highly efficient technology, does not require elements that are hard to secure, other material-based approaches are necessary. CZTS is a sustainable process, but with constraints in the quality and reproducibility of used materials. New developments in defect passivation, interface, engineering and compositional tuning are encouraging to reduce this performance gap (Kumar et al., 2021). The next generation applications in achieving efficiency, stability, and sustainability of ternary semiconductors have to be balanced in order to make ternary semiconductors a dependable sub unit in tandem devices.

Table 3.1: Key Properties of Ternary Semiconductors

Property	CIGS (Cu(In,Ga)Se ₂)	CZTS (Cu ₂ ZnSnS ₄)
Band Gap (eV)	1.0–1.7 (tunable)	~1.5 (ideal for PV)
Absorption Coefficient	>10 ⁵ cm ⁻¹	~10 ⁴ cm ⁻¹
Record Efficiency	>23%	~12–13%
Elemental Abundance	Limited (In, Ga scarce)	Earth-abundant, eco-friendly
Common Applications	Thin-film, flexible PV	Sustainable thin-film PV
Tandem Role	Top or bottom absorber	Bottom absorber (with Se)

Figure 3.1: Band Gap Tuning in CIGS and CZTS



4. Quaternary Compound Semiconductors

The accepted quaternary semiconductors, notably $\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe) and $\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$ (CIGSeS) have been considered as absorber materials towards thin-film photovoltaics. These compounds enhance the merits of ternary semiconductors with more compositional freedom, narrower band-gaps, lattice-match, and expanded repertoire in tandem solar cells (Chen et al., 2020).

$\text{Cu}_2\text{ZnSn}(\text{S},\text{Se})_4$ (CZTSSe)

A solid solution of CZTS and CZTSe, CZTSSe is made by reacting a certain ratio of the sulfur to sulfur selenium forming the desirable band gap. This ratio can be varied to tune the band gap between the potential range of 1.0 eV (selenium-rich) to 1.5 eV (sulfur-rich) (Yang et al., 2022). This tunability also gives CZTSSe special versatility to tandem configurations to allow CZTSSe to be used as a bottom cell absorber with wide-band-gap substances. CZTSSe still enjoys the merits of earth-abundance and non-toxicity allowing it to be a green substitute of indium- and gallium-based compounds. Nevertheless, issues like

cation disorder, tailing in bands and the formation of a secondary phase are hindering factors to high efficiency. Present record single-junction efficiencies are approximately 13% which is less than CIGS, but still enhances into defect passivation as well as interface engineering (Green et al., 2023).

$\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$ (CIGSeS)

CIGSeS is a quaternary CIGS alloy, where a better band-gap control is given by use of incorporation of sulfur. CIGSeS can be tuned to a band gap of between 1.0 and 2.0 eV correspondingly (selenium-rich and sulfur-rich respectively), providing one of the broadest ranges of band gaps of any type within a family of semiconductor compounds (Jackson et al., 2016). This has allowed designers to make optimizable absorbers for both top and bottom sub-cells when designing tandem structures. Besides, the addition of sulfur may enhance compatibility and stability of materials in lattices and compatibility with the transparent conductive oxides to minimize recombination at the interfaces. Nonetheless, CIGSeS shares

the scarcity issues that CIGS has especially because of the indium and gallium substances used.

Roles in Tandem Architectures

Quaternary semiconductors extend the design space of multi-junction solar cells via control of optical and electrical properties with great accuracy. An example is that a tandem of a wide-band-gap CIGSeS top cell (approx 1.7 eV) and a low-band-gap CZTSSe bottom cell (approach 1.0 - 1.2 eV) can be able to have nearly optimum current matching. Theoretical efficiencies of such designs are above 30 percent, but in practice, devices are still not able to perform because of material defects and optimally design interfaces (Geisz et al., 2020).

The Challenges and Opportunity

Even though quaternary compounds have distinct benefits in tunability and sustainability, more complexities are introduced with them. In order to minimize recombination losses, it is important to control stoichiometry, cation ordering and defect chemistry. The recent studies have proved perspectives in alkali metal doping (e.g., Na, K), refinement of buffer layers and novel ways of deposition including co-evaporation, atomic layer deposition as a solution to enhance the quality of materials (Kumar et al., 2021). In case there is an approach of such issues, quaternary absorbers would be an important part of scalable tandem technologies.

Table 4.1: Key Properties of Quaternary Semiconductors

Property	CZTSSe	CIGSeS
Band Gap (eV)	1.0–1.5 (tunable via S/Se)	1.0–2.0 (tunable via S/Se, Ga)
Absorption Coefficient	$\sim 10^4 \text{ cm}^{-1}$	$> 10^5 \text{ cm}^{-1}$
Record Efficiency	$\sim 13\%$	$> 22\%$
Elemental Abundance	Earth-abundant, eco-friendly	Limited (In, Ga scarce)
Tandem Role	Bottom absorber ($\sim 1.0\text{--}1.2 \text{ eV}$)	Top absorber ($\sim 1.7 \text{ eV}$)
Key Challenges	Disorder, secondary phases	Scarcity, interface issues

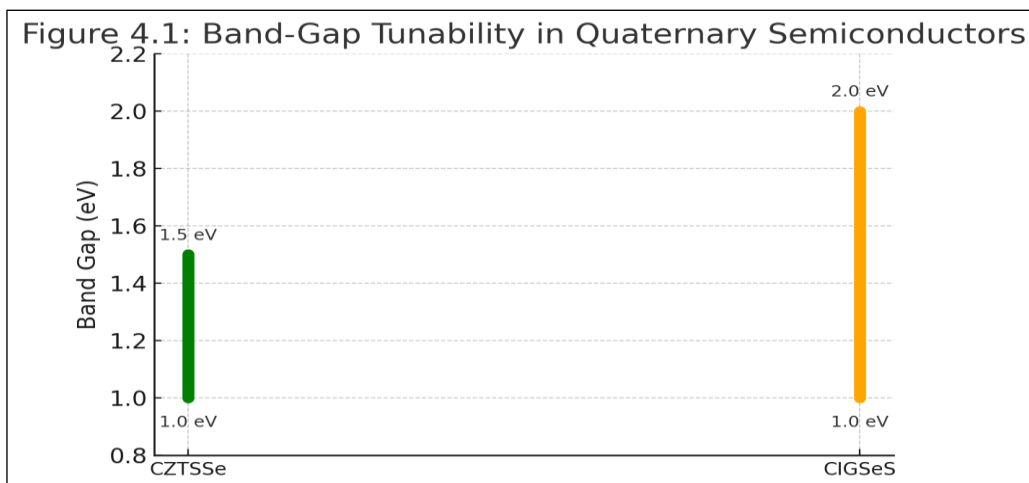


Figure 4.1: Band-Gap Tuning in Quaternary Semiconductors

5. Dual Types of Ternary and Quaternary Tandem Architectures

A key focus in becoming a potential concentration of the study of thin-film photovoltaics has been design of tandem solar cell using ternary and quaternary compound semiconductors. They use the complementary gaps between the different materials like CIGS, CZTS, CZTSSe, and CIGSeS to take control of a wider spectrum of the sun and thus exceeding the efficiency limits of single-junction devices (Green et al., 2023).

Monolithic Tandem Designs

In monolithic tandem cells, there are many absorber layers stacked together with an interconnect - transparent tunnel junctions. As an example, a tandem cell built with CIGS used as the top and CZTS as the bottom cell, which utilizes both 1.7 eV and 1.0-1.2 eV as their respective band-gap combinations offers an ideal situation to develop a dual-junction device (Almansouri et al., 2018). CIGSeS and CZTSSe can also be used in the same manner as the sulfur to selenium ratio can be fined to achieve maximum spectral coverage and current matching. The good thing on monolithic tandems is that, they are small and very high efficiency can be obtained, but very accurate lattice and band placement is essential to eliminate interface recombination.

Mechanical Stacks of Tandems

Mechanical stacking of sub-cells is also an alternate and the cell may be made in isolation and then optically or electrically connected. As an illustration, a CZTSSe/Si tandem cell will

stack kesterite on silicon as a top cell and silicon as a bottom absorber and take advantage of silicon, which is both highly stable and relatively cheap. In this approach, the lattice disparity problem is eliminated, but there are problems related to optical losses, the integration of modules, and expenses in general (Geisz et al., 2020).

Band-Gap Engineering at Tandem

The benefit of ternary and quaternary semiconductors is in the ability to tune the band-gap. Researchers can tune adjusting the Ga/(In+Ga) ratio of CIGS or S/Se ratio of CZTSSe to gain current matching in between two sub-cells which is important in maximizing tandem cell. To demonstrate, one 1 CIGSeS top cell (~1.7 eV) + CZTSSe bottom cell (~1.0 eV) has been simulated to reach approximately 30% efficiencies (Chen et al., 2020).

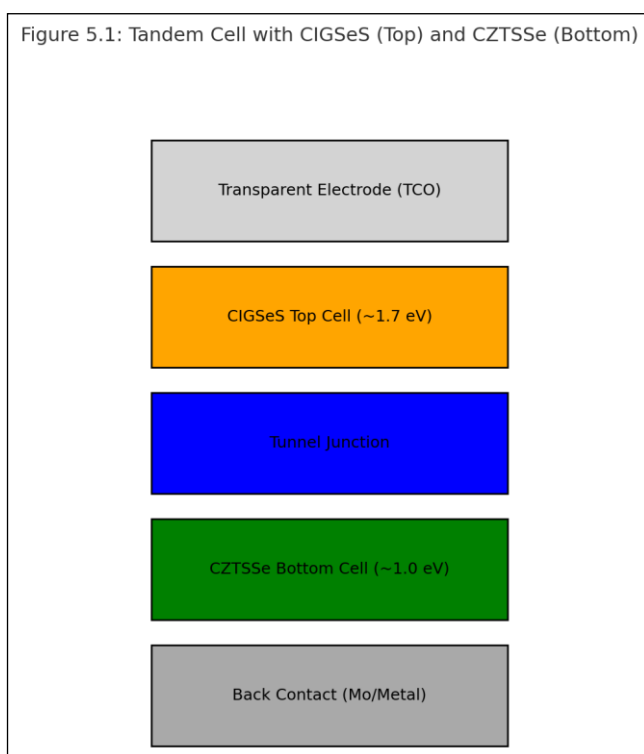
Integration Challenges

Tandem architectures have a few challenges in as much as they promise good prospects. Creating flawless junction, ordering cations in kesterites, and the reduction of interface recombination are currently underway. In addition to this, long-term thermal and photostability is essential to commercialization. The development of advanced fabrication methods, like co-evaporation, atomic layer deposition (ALD), and solution based methods, is involved to overcome these issues (Kumar et al., 2021).

Table 5.1: *Examples of Tandem Architectures with Ternary and Quaternary Semiconductors*

Tandem Design	Top Cell (Band Gap)	Bottom Cell (Band Gap)	Potential Efficiency	Key Challenges
CIGS / CZTS	CIGS (~1.7 eV)	CZTS (~1.1 eV)	~28–30% (theoretical)	Voc deficit in CZTS
CIGSeS / CZTSSe	CIGSeS (~1.7 eV)	CZTSSe (~1.0–1.2 eV)	~30% (simulated)	Disorder, recombination losses
CZTSSe / Si	CZTSSe (~1.5 eV)	Si (~1.1 eV)	~27% (reported)	Optical coupling losses
Perovskite / CZTSSe	Perovskite (~1.6–1.8 eV)	CZTSSe (~1.0 eV)	>30% (predicted)	Stability of perovskite

Figure 5.1: Schematic of a Tandem Solar Cell with Ternary and Quaternary Absorbers



6. Optimization of Energy Conversion at Band-Gap Engineers

Tandem solar cell design is based on band-gap engineering. This can be achieved by stricter adjustments of the energy band gaps of the absorber materials to optimize the current generation rates between the sub-cells, reducing the recombination and optical losses, and resonant conversion of energy so that the total energy conversion efficiency is at its

maximum (Shockley and Queisser, 1961). Compositional tuning (e.g., Ga/In and S/Se ratios) is an option in the case of ternary and quaternary type semiconductors such as CIGS, CZTS, CIGSeS, and CZTSSe allowing broad seek-ho where each concept gives uniquely flexible spectral characteristics that make it highly versatile in tandem manufacture.

Theoretical Framework

Shockley Queisser limit gives one a basis on which to relate band gap to the photovoltaic efficiency. One absorber with a band gap = 1.34 eV is allowed to reach high theoretical efficiency = 33 per cent in AM1.5 illumination (Green et al., 2023). But even with two absorbers, layered with band gaps of about 1.7 eV (top) and 1.0 eV (bottom); some predicted absence of theory efficiencies of about 42 can be realized. By reaching three optimized band gap absorbers (around 1.9, 1.4, and 1.0 eV), this result goes to greater extremes, up to above 50% (Almansouri et al., 2018). These values explain the significance of the compositional flexibility in attaining the high-performance tandem devices.

Compositional Tuning

CIGS/CIGSeS: Ga/ (In +Ga) ratio governs the band gap of 1.0-1.7 e V. Higher proportion of Ga has a positive effect on the band gap and makes the material an apt top cell with wide band gap (Jackson et al., 2016).

CZTS/CZTSSe: The activation entails the band gap precision based on S/Se range about 1.0 1. 5 eV. Compositions with Selenium-rich (~1.0 eV) are suited to bottom cell, and sulfur-rich (~1.5 eV) are top ones (Yang et al., 2022).

This tunability enables the researcher to come up with tandem configurations that have almost optimal current matching. An example is the efficiency of simulations of CIGSeS/CZTSSe tandem with almost 30 percent when band gaps are carefully matched (Chen et al., 2020).

Passivation of Defects and Interface Engineering

Composition is not the only technique of band-gap engineering. Band tailing is removed by defect passivation (e.g. by doping with alkali, such as Na, K) and band alignment between the absorbers and transport layers by interface optimization. These improvements inhibit the recombination leading to an increase in the open-circuit voltage (Voc), and the fill factor (Todorov et al., 2013).

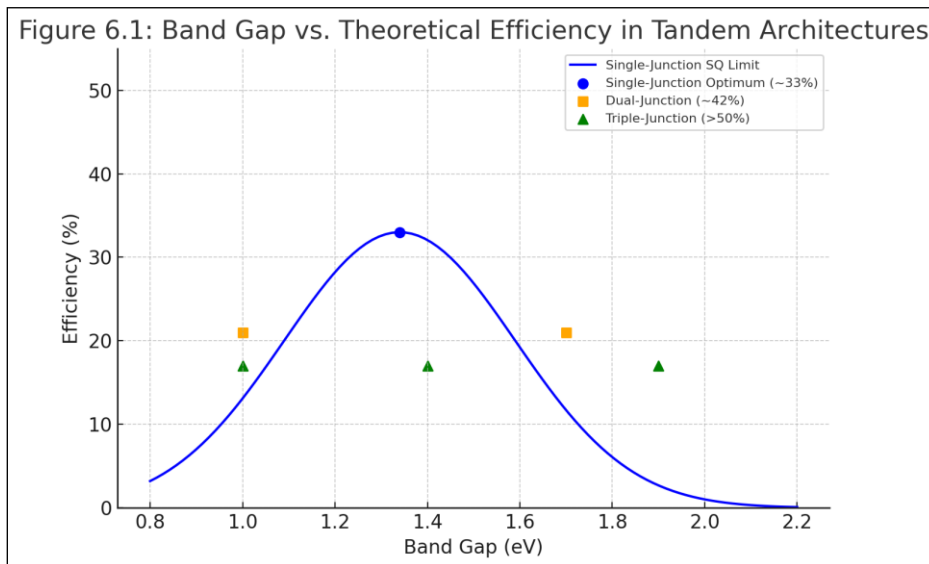
Future Prospects

Some of the emerging options involve incorporating quaternary absorbers with perovskites, taking advantage of the wide-band-gap adjustability of perovskites and stability of chalcogenides. This integrative model can enable efficiencies that are more than 35 percent with low-cost and scalable production possibilities (Geisz et al., 2020).

Table 6.1: Optimal Band-Gap Combinations for Tandem Solar Cells

Tandem Type	Top Cell Band Gap (eV)	Bottom Cell Band Gap (eV)	Theoretical Efficiency
Single-Junction	~1.34	—	~33%
Dual-Junction	~1.7	~1.0	~42%
Triple-Junction	~1.9	~1.4 / ~1.0	>50%
CIGSeS/CZTSSe Tandem	1.7	1.0–1.2	~30% (simulated)

Figure 6.1: Band Gap vs. Theoretical Efficiency



7. New Developments and Recent Findings

Efficiency, stability, and material quality have been characterized as some of the recent advances realised in tandem solar cells based on the use of ternary and quaternary compound semiconductors. Scholars have put more efforts in incorporating materials like CIGS, CZTSSe and CIGSeS into monolithic or mechanically stacked tandem devices, as has been exploiting their controllable bandgaps to expand spectral coverage and enhance current matching (Green et al., 2023).

Efficiency Milestones

During the past ten years, considerable advances have been realized on both single-junction and tandem devices. With optimized Ga composition and defect passivation, CIGS single-junction solar cells have reached record efficiencies of over 23 (Jackson et al., 2016). Equally, the CZTSSe-based devices have obtained (albeit with marginal gains) a reaching of the 13% efficiency, along with an increase in defect engineering and interface quality (Yang et al., 2022). CIGSeS/CZTSSe and other tandem combinations have been shown to have 30-percent simulated efficiencies although experimental realizations

are generally smaller and recombination-related problems and inhomogeneity of materials (Chen et al., 2020).

Processing and Counterfeiting Propaganda

Development of deposition processes has been a very important issue in the enhancement of performance of devices. Solution-based technology has been used to complement both traditional co-evaporation and sputtering methods to allow the low-cost and large-area execution such spin coating, inkjet printing, and chemical bath deposition (Kumar et al., 2021). In addition, alkali metal (Na, K, Rb Cs) addition in CIGS and CZTSSe has enhanced grain purification, defect density and open-circuit voltage (Voc). These chemical additions have assisted in combating lack of voltage that had been a setback to efficiency.

Junction and Interface Engineering

An important enabling factor to monolithic tandems is the creation of constructive tunnel junctions. It has been demonstrated that transparent recombination layers like highly doped ZnO or indium tin oxide (ITO) are researched to guarantee effective carrier

transport without optical losses (Geisz et al., 2020). Passivation layers, including ultrathin Al₂O₃ Silva have also been implicated to reduce interface recombination across absorber-buffer interfaces and give significant device performance improvements as a result.

Simulation and Modeling

Together with experimental innovations, numerical simulating devices such as SCAPS and TCAD have played very vital roles in forming the behavior and the selection of materials of various devices. The models enable researchers to test the correct matching conditions, band-gap combinations and defect states and can optimize the experiments faster. It has been predicted that CIGSeS/CZTSSe tandem optimization can be as efficient as 30 and perovskite/kesterite hybrid can be even

more efficient, at 35, on a standard day (Almansouri et al., 2018).

Difficulties and Future Research Problems

Although some positive outcomes can be seen, a number of problems are present. Open-circuit voltage corruptions of CZTSSe devices are severe because they are caused by cation disorder and band tailing. However efficient, CIGSeS is limited by the dependence on such limited elements as indium and gallium. What is more, it is hard to scale the laboratory devices to the level of industrial functioning and continue to work on these devices and remain stable. However, current studies on defect passivation, new buffer layers, and hybrid tandems including perovskites are likely to get efficiencies high enough to approach the theoretical limits.

Table 7.1: *Recent Advances in Compound Semiconductor Tandem Solar Cells*

Material/System	Band Gap (eV)	Record Efficiency	Key Advancements	Challenges
CIGS (single-junction)	1.0–1.7 (tunable)	>23%	Ga/In tuning, alkali doping, passivation	Scarcity of In, Ga
CZTSSe (single-junction)	1.0–1.5 (tunable)	~13%	S/Se tuning, interface optimization	Voc deficit, cation disorder
CIGSeS/CZTSSe Tandem	1.7 / 1.0–1.2	~18–20% (exp.), ~30% (simulated)	Band-gap engineering, tunnel junctions	Defects, recombination losses
CZTSSe/Si Tandem	1.5 / 1.1	~27% (reported)	Mechanical stacking, interface design	Optical coupling, scalability
Perovskite/CZTSSe Tandem	1.6–1.8 / 1.0	>30% (predicted)	Hybrid integration, wide tunability	Stability of perovskite layers

8. Challenges

Even though amazing breakthroughs have been recorded in the area of tandem solar cells which utilize ternary and quaternary semiconductors, there are still a few unresolved issues that impede the large scale rollout of such systems and their deployment

in practice. These issues are at both material level, challenges in integrating devices and also having issues over long term stability.

Voc Deficit/ Defect States

The enduring loss of open-circuit voltage (Voc) has been one of the major challenges in compound semiconductors especially the

CZTSSe material. The experimental Voc values are dismal in comparison to theoretical values even with near perfect band gap. This discontinuity is due to deep-level defects, cation disorder, and band tailing, which also form recombination sites in the absorber layer (Yang et al., 2022). As an example, the antisites (like CuZn and ZnCu) in CZTSSe create localized states around the band edges and accordingly cause non-radiative recombination to occur showing loss of efficiency.

Secondary Phase Formation

The other serious problem is that in the material growth, there is the development of the secondary phases. ZnS, SnS, and MoS₂ phases also commonly occur in CZTS and CZTSSe along with the main absorber. These secondary stages do not only shrink device performance because of shunts in addition to disrupting reproducibility as well as mass production. Even though synthesis methods have been developed to overcome some of these problems including co-evaporation, solution processing, and sulfurization/selenization control, full elimination of secondary phases has been unsuccessful (Polizzotti et al., 2013).

Material Scarcity and Cost

CIGS and CIGSeS have very promising efficiency, though they are dependent on indium and gallium, which are very rare; and very costly. This dependency poses a question of long term sustainability particularly in case such technologies were extended to produce multi-gigawatts. As compared, CZTS-based materials are more sustainable, as they are made of high-abundant elements, but their performance deficit generates a trade in maintaining efficiency against sustainability. To resolve this dilemma, it will be necessary to either enhance the consumption of the

currently available materials in the Earth that can tolerate defects, or to find new compounds that merge high performance with large elemental content.

Tunnel Junction and UISE

Tunnel junctions are important electrical connectors that happen in monolithic tandem architecture between sub-cells. Faults at these junctions or defects or poor alignment of bands resulting from optical absorption to an excessive degree can greatly limit tandem performance. Doped and defect passivated surfaces are still technologically difficult to achieve ideal tunnel junctions (Geisz et al., 2020). Moreover, since lattice match between various sub-cells is frequently problematic, this leads to dislocations which serve as recombination sites, which compromises theoretical efficiency potential of tandem devices.

Stability and Reliability

Another imminent concern is the stability of tandem devices in the long run. As temperature rises and is worn out or degraded over an extended period of time defect propagation, phase wall segregation, or interfacial reactions reaction are usually enhanced. Such as, fluctuations in band-gap with time in sulfur-selenium CZTSSe the layers or gallium redistribution in CIGS layers can be resultant. Moreover, the systems of perovskite top cells and kesterite or CIGS bottom cells prove to have an additional challenge because perovskites are extremely phobic to water, air as well as temperature (Yang et al., 2020).

Scalability and Manufacturing

Lastly, the ability to scale laboratory-scale devices (often <1 cm²) to large modules without limiting their performance is one of the primary impediments. It is still challenging to preserve uniform composition, porosity, and

defect monitoring of large scale. Other possible methods of deposition like solution processing or inkjet printing can prove to be cost effective, although this requires demonstration of both reproducibility and long term stability before these can be utilized by manufacturing industries.

9. Future Prospects

The medium-term future of tandem solar cells based on ternary and quaternary agent semiconductors is bright subject to resolving the current difficulties in the sphere of materials and integration. Future developments in the band-gap engineering and interface optimization as well as defect passivation are also likely to receive decisive contributions towards the reduction of the gaps between theoretical and practical efficiencies.

The most interesting direction of the future is the creation of hybrid tandem layouts, and especially with the top cells being perovskite and the bottom cells being kesterite (CZTSSe) or CIGSeS. It has the advantage of high tunability and efficiency potential of perovskites and stability and earth-abundant composition of quaternary semiconductors (Geisz et al., 2020). With stability issues in perovskites sorted out, hybrid tandem may achieve over 35 percent same making it equal to traditional silicon technologies.

The future of tandem photovoltaics will also be determined by sustainability. Tandems based on CZTSSe provide an alternative to ramp indium and gallium devices which are more environmental friendly. Future efforts in acting as efficient dopant engineering and control in phase purity and refined deposition methods might greatly enhance their efficiency such that they can be used as dependable components in PV large power modules.

In addition, the use of tandem solar cells in building-integrated photovoltaics (BIPV), flexible substrates, and the portable energy systems has further enabled their application in other entirely new ways that are not limited to just solar farms. This versatility would be quick to adopt in the urban regions where space is few but energy requirements are high.

A breakthrough of compound semiconductor tandems will be attained in the long-term with efficiencies of >30% being achieved with stability, scalability and low costs. As the material novelty collides with device orchestrating and reproductively large-scale assembly, these technologies are ever going to take centre stage to the destiny of renewable power structures.

10. Conclusion

Ternary and quaternary compound semiconductor tandem solar cells Tandem solar cells remain a revolutionary direction forward through the efficiency barriers of the single-junction devices. CIGS, CZTS, CIGSeS and CZTSSe among materials possess a unique advantage in charge of tuning the band-gap, intensive absorption, and ability to be covered by acceptable thin-film technologies. Slann Communications Complementary absorber Recent theoretical work by stacking absorbers with complementary band gaps shows a potential of going to over 40 percent spectro-electronic efficiency in tandem PV architecture designs, and initiates the potential of next-generation photovoltaics on that basis.

Notwithstanding the promise, there are several issues that still exist. The attention of these devices is hampered by voc deficits, defect states and the formation of second phase as well as, the institution of long term stability. Also, the scarcity of elements relied on by CIGS and CIGSeS is the reason to develop the sustainable alternative and CZTS-based

systems, despite being environmental friendly are still underperforming in their efficiency.

In the future, it has been shown that the incorporation of best defect passivation techniques, tunnel junctions design, and hybrid tandems with the perovskites can provide good solutions. Provided that these innovations are successful in bringing to life laboratory-scale progress into non-laboratory scale devices, ternary and quaternary compound tandem solar cells may become a viable, long term, user-friendly and high-efficiency photovoltaic mechanism.

In the long term, such materials will be used by their combined efficiency, sustainability, and scaling nature to dictate their role in the future in the global renewable energy context.

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