CZTS nanocrystals: a promising approach for next generation thin film photovoltaics

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Cu₂ZnSn(S,Se)₄ (CZTSSe) has received considerable attention as a material capable of driving the development of low-cost and high performance photovoltaics. Its high absorption coefficient, optimal band gap, and non-toxic, naturally abundant elemental constituents give it a number of advantages over most thin film absorber materials. In this manuscript, we discuss the current status of CZTSSe photovoltaics, and provide a comprehensive review of Cu₂ZnSnS₄ (CZTS) and Cu₂ZnSnSe₄ (CZTSe) nanocrystal (NCs)-based fabrication methods and solar cell characteristics. The focus will be on the relevant synthetic chemistry, film deposition, and the production of high efficiency photovoltaic devices. Various colloidal synthesis routes are currently used to form the highest quality CZTSSe film from the nanocrystals with controllable phase, size, shape, composition, and surface ligands. A variety of recipes are summarized for producing nanocrystal inks that are appropriate for forming CZTSSe absorber materials with a wide range of controllable optoelectronic properties. Deposition and post-processing, such as annealing and selenization treatments, play an important role in defining the phase and structure of the resulting material. Various film treatment strategies are outlined here, and their resulting material quality, device performance, and dominant photovoltaic loss mechanisms are discussed. Suggestions regarding needed improvements and future research directions are provided based on the current field of available literature.

Broader context

Cu₂ZnSn(S,Se)₄ (CZTSSe) with its high absorption coefficient, optimal band gap, and non-toxic, naturally abundant elemental constituents has a number of advantages over most thin film absorber materials. Nanocrystal dispersions of CZTS represent a unique method for producing photovoltaic quality absorbers. A nearly unprecedented level of control in designing and producing precursor materials and inks prior to all aspects of film deposition enables the assembly of high quality kesterite crystallites in a rational way. With the preformed high quality kesterite structure, the nanoparticles approach has been demonstrated to reduce the number of impurity phases and defects present in the final film. To date, solar cells based on CZTS nanoparticle inks have reached power conversion efficiencies of nearly 10%, putting them quite close to the record 11.1% efficiency for this material system. Further improvement will be a better understanding of the myriad of defect properties arising from the complex cation ordering arrangement, and the ultimate success of this fabrication strategy relies on the synergistic optimization of both material synthesis and film treatments. The nanocrystals approach and relative earth abundance of these material systems stand as stiff competition for the widespread adoption of CZTS solar cells and modules.

1 Introduction

To have a real impact on worldwide power consumption (~terawatt (TW)), photovoltaic materials need to be cost effective, earth abundant, and offer a long functional lifetime and high power conversion efficiency. Direct band gap metal chalcogenide thin film PV technologies demonstrate the potential to reduce production costs for both raw materials and processing requirements.¹,² Despite the promise of Cu(In,Ga)S₂ (CIGS) and CdTe thin film technologies,³⁻⁷ the scarcity of elements such as indium and tellurium may limit their potential for production on the TW level.³ With indium replaced by zinc and tin, copper zinc tin chalcogenide (CZTSSe) is emerging as a leading candidate to further advance thin film PV to its full potential. Consisting solely of earth abundant, non-toxic, and inexpensive elements, CZTSSe offers a high absorption coefficient of ~10⁴ cm⁻¹ with an adjustable band gap that can range from 1.0 to 1.5 eV to favorably match the solar spectrum.⁴⁻¹⁰ CZTSSe thus opens the door for both economic and ecological thin film device production without limitations from raw materials. Rapid progress in kesterite CZTSSe material development has advanced its conversion efficiency from 6.8% to beyond 11% in the last few years.¹¹⁻²⁰
For metal chalcogenide based materials, the relatively high tolerance of structural and electronic defects relaxes the strict requirements for carefully controlled vacuum-based deposition.\cite{21,22} Non-vacuum based approaches thus have the opportunity and motivation to deposit high quality films in a cost effective way. With respect to CZTSSe, solution processing has the potential to control phase formation and to demonstrate high performance devices comparable to or even better than those produced by vacuum-based approaches.\cite{13,15,16} The success of CZTSSe processing is directly associated with controlling the formation of the kesterite phase, a goal that poses unique material challenges.\cite{18} Perhaps the most difficult aspect of CZTSSe deposition, especially when compared with CIGS, is that single-phase kesterite exists within a much smaller stoichiometry range, normally Cu-poor (Cu/(Zn + Sn) = 0.8–0.9) and Zn-rich (Zn/Sn = 1.1–1.4).\cite{23,24} The volatile nature of some of its elemental constituents and related binary phases (such as tin chalcogenide, zinc metal, etc.) further impedes attempts to create phase purity within deposited films, especially for techniques associated with high temperatures and vacuum conditions.\cite{25} This makes sophisticated compositional control a key prerequisite for any synthetic route to fabricate high performance CZTSSe films.\cite{13,26,28} Solution based approaches that form the target phase at lower temperatures currently can therefore offer a number of advantages to control pure kesterite phase formation, and allow for the continued development of improved control over the phase and defect properties of this complex material family.

A reliable synthesis route is essential for achieving a high quality CZTSSe phase to control the defect properties that ultimately govern device performance. This article provides an introduction to the current status of nanocrystal-based fabrication routes to produce CZTSSe solar cells, mainly based on annealed CZTSSe as the absorber layer. The various colloidal synthesis routes of CZTSSe are broken down in terms of size, composition, shape and phase control of the nanocrystals. Recent progress in film formation and device performance is then summarized, including the latest progress in high performance device fabrication with a focus on film processing, device physics, and defects study. Finally a discussion on flexible devices and a future outlook for CZTSSe nanoparticle devices are provided.

## 2 CZTS nanocrystal based approach for photovoltaic devices

CZTS nanocrystal-based approaches start with the controlled synthesis of nanocrystals and end with the deposition and post-treatment of films using the resulting inks.\cite{27} Compared with hydrazine-based processing,\cite{11} which uses the explosive solvent hydrazine during ink formation and film deposition, the preparation of CZTS nanocrystals only requires the involvement of common organic solvents and precursors. In addition, the capability of mass production of nanocrystals, together with...
their compatibility with ultrahigh throughput deposition techniques such as printing and casting, each of which are well-established industrial procedures, enables CZTS nanocrystal-based techniques for terawatt capacity module production.

As solution-phase processes, CZTS nanocrystal-based approaches have the potential to control phase formation and to demonstrate high performance devices comparable to or even better than those produced by vacuum-based methods. More importantly, using solution processed CZTS nanocrystals is currently the only approach that enables phase formation to occur prior to film deposition. For other solution-based approaches, including molecular solutions and mixed solution/particle slurries, the phase formation requires one or more solid state reactions to take place after the film has been dried. Due to the difficulty of diffusion in the solid state, the CZTS film could experience a much greater tendency to decompose into binary, ternary, and quaternary phases due to compositional nonuniformities throughout the film. The nanocrystal approach, with phase formation taking place in the liquid phase in a carefully controlled environment, allows for each constituent far greater diffusivity values in order to overcome the activation energy barrier to reach the thermodynamically stable phase. In addition, other solution-phase techniques lead to some unexpected residues left over in deposited films, which can significantly influence device performance.\textsuperscript{29} In contrast, although the synthesis of CZTS nanocrystals is based on similar precursors to those of other solution processes, many of the impurities can be removed during post-synthesis washing treatments before the final ink is made (Fig. 1).

It is well known that the CZTS, which is derived from the structure of CuInS\(_2\) (CIS\(_2\)) by replacing two In atoms with one Zn and one Sn, is significantly more complex in its cation ordering arrangements as a quaternary material (Fig. 2).\textsuperscript{30} The complexity of this quaternary system manifests in an intense competition between the CZTS phase and its binary components, e.g., CuS, ZnS, SnS, or ternary components, such as Cu\(_2\)SnS\(_4\). In addition, a variety of point defects are easily formed due to the similar radii of the various ionic species. These include vacancies, antisites, and interstitials, e.g., Cu\(_{\text{Zn}}\), V\(_{\text{Cu}}\), V\(_{\text{Zn}}\), Zn\(_{\text{Sn}}\), Cu\(_{\text{Sn}}\), many of which can result in trap states deep within the band gap. A processing method capable of solving these problems will need to provide flexible synthetic tools for engineering the phase and point defects of the CZTS absorber layer while maintaining compatibility with low cost and scalable manufacturing. Nanocrystal approaches provide a flexible chemical tool to control the nucleation and crystal growth of the desired materials, and can readily incorporate some extrinsic dopants to achieve grain boundary passivation and defect property engineering. Similarly, the separation of crystallite formation and grain growth allows for increased flexibility in post-deposition processing, and can dramatically benefit the performance of any resulting devices (Fig. 1).

Nanocrystal based solar cells can be divided into two general categories. One uses little or no heat treatment during device fabrication, preserving the nanocrystalline properties of the absorber material. Generally, the efficiency of nanocrystal devices based on low temperature processing is limited by the large concentration of interfaces in the absorber films, due to the extremely small size of the nanocrystals. For quaternary CZTS materials, it is quite difficult to achieve a promising efficiency by this method, due to the extensive trapping of carriers in the nanocrystal film, as well as a generally shallow space-charge region.\textsuperscript{32} Further discussion of low temperature CZTS or CZTS hybrid solar cells can be found in Section 4.6.

A far more successful approach for processing multinary chalcogenide nanocrystal based solar cells is through the high temperature annealing of the as-deposited films, which strongly enhances grain growth when conducted in a sulfur or selenium atmosphere, typically referred to as sulfurization and selenization, respectively. Annealed CZTSSe films routinely reach grain sizes on micron scales, rather than the nanometer-scale size of the original nanoparticles. The use of annealed CZTSSe films also significantly decreases the presence of surface defects and grain boundaries, contributing to far more favorable conduction pathways for photogenerated carriers, and a dramatic improvement of every photovoltaic parameter, including short circuit current, open circuit voltage, and fill factor. Facilitated by the accumulated experience on CZTSSe solar cells gained using other approaches,\textsuperscript{31,35} research on CZTS nanocrystals has made tremendous progress since the first reported synthesis of CZTS nanocrystals in 2009.\textsuperscript{27} It is reported that the nanocrystal based CZTSSe solar cell has already reached a power conversion efficiency of 9.85% as of 2012, as a result of optimization of the synthesis of CZTS nanocrystal inks and the corresponding film engineering.\textsuperscript{32}

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**Fig. 1** Schematic diagram of the fabrication of CZTS absorber layers from nanocrystal ink and molecular solution.

**Fig. 2** Schematic illustration of the origin of Cu\(_2\)ZnSnS\(_4\) and its kesterite structure.
3 Nanocrystal based CZTSSe absorber layer formation

The fabrication of effective CZTSSe films requires synthesis reactions that produce nanocrystals with controllable composition, phase, surface structure and dispersibility in appropriate solvents. CZTSSe absorber layer formation has developed along three major approaches, including the synthesis of colloidal quaternary CZTS or CZTSe nanocrystals based on thermolysis techniques, the formation of CZTSSe films from binary or ternary colloidal nanocrystals, and the synthesis of hydrophilic CZTS nanocrystals based on solvothermal methods. Hydrophobic colloidal nanocrystals are composed of an inorganic crystalline core with specified composition and a crystal phase that is covered with a chemisorbed layer of organic ligands, e.g., oleylamine (OM), to prevent aggregation and provide dispersibility in nonpolar solvents. Currently, impressive device performances have been achieved based on colloidal nanocrystals, and both quaternary CZTS or the combination of binary ZnS and ternary Cu2SnS4, leading to profound conversion efficiency (PCE) values of 9.85 and 8.5, respectively. Hydrophilic CZTS nanocrystals are currently not as popular as their hydrophobic relatives, with ethylene glycol and PVP being a common solvent and ligand system used to provide good dispersibility in polar solvents. Unfortunately, the resulting nanoparticles are generally reported to produce inferior device performance, due to the difficulty in high quality film formation, compared with that of hydrophobic nanocrystal based devices (Fig. 3).

Since colloidal CZTS nanocrystal based solar cells have demonstrated some of the most promising performance, compared with other nanocrystalline CZTS materials, we will mainly discuss the synthesis of hydrophobic nanocrystals, including CZTS, CZTSe, and Cu2Zn(Sn,Ge)S4 (CZTGeS), as well as the chemical tools and pathways available for controlling the size, shape, composition, and phase of the reaction products. For comparison purposes, hydrophilic CZTS nanocrystals will be used as examples to investigate the underlying reaction mechanism and characteristics of the as-obtained nanocrystals. The colloidal nanocrystals are synthesized by burst nucleation from molecular precursors in long chain coordinating solvents, followed by controlled particle growth. Currently, the colloidal chemistry route is widely accepted for making a variety of semiconductor nanocrystals, including II–VI, III–V, I–VI, IV–VI and group IV materials. Similarly, a wide variety of ternary and quaternary compounds can also be synthesized, including CuInS2, CuInSe2, CuGaSe2, CIGS, and CZTS.

3.1 CZTS nanocrystals

The synthesis of colloidal CZTS nanocrystals starts with precursors, carefully chosen Cu, Zn, and Sn compounds, being dissolved in long chain coordinating solvents followed by burst precipitation and controlled growth after mixing with a sulfur source at the desired temperature. This method can generate a quaternary compound semiconductor with kesterite crystal structure of high phase purity at good yield. A variety of target compositions can be easily achieved by adjusting the ratio between each metallic precursor. The phase of the CZTS nanocrystals can be varied from the traditionally obtained CZTS kesterite or stannite phases, which feature a tetragonal unit cell, to the wurtzite phase with a hexagonal crystal cell. In order to obtain the kesterite phase, which is the favorable phase for CZTS in photovoltaic applications, it is necessary to carefully control the chemical environment during synthesis in terms of the different coordination strength and reactivity between the various ligands and cations in solution. The dispersibility of CZTS nanocrystals in nonpolar solvents can also be improved by the addition of suitable surfactants. The majority of previously reported results suggest that chloride, acetate, and acetylatedonate compounds are effective copper, zinc, and tin precursors, despite their different dissociation capabilities in coordinating solvents. By far the most widely used solvent is oleylamine, with its high boiling point and coordinating ability to chalcogenide compounds, while trioctylphosphine oxide (TOPO), oleic acid (OA), and octadecene (ODE) are also occasionally employed. Sulfur can be incorporated into the reaction system by dissolving elemental sulfur directly into oleylamine; meanwhile, other sulfur sources, such as dodecanethiol (DT) can also be used during synthesis to provide the sulfur component, and control crystal growth as well.

The original synthesis of CZTS nanocrystals was by hot injection of a solution of elemental sulfur in oleylamine into a solution containing 1.5 mmol copper(II) acetylacetonate, 0.75 mmol of zinc acetylacetonate, and 0.75 mmol of tin(IV) bis(acetylacetonate) dibromide in oleylamine at 225 °C. Fig. 4a shows a transmission electron microscopy (TEM) image of the as-synthesized CZTS nanocrystals. CZTS nanocrystals synthesized using this method exhibit mild polydispersity, with most of the nanocrystals falling in the range 15–25 nm. Based on this synthetic recipe and after adjusting the stoichiometric metal precursor ratio to become Zn-rich and Sn-poor, high quality CZTS nanocrystals were achieved and produced a photovoltaic efficiency of 7.2% in 2010 just one year after the first reported synthesis of kesterite nanocrystals. Besides the original synthesis protocol, subsequent progress has led to the development of various other recipes for forming high quality crystals, with changeable precursor types and varying reaction temperatures and times, different precursor injection modes, and various other routes for incorporating sulfur into the reaction. The majority of reported results emphasize the

Fig. 3 Schematic diagram of the synthesis of Cu2ZnSn(S,Se)4 nanocrystals via the thermolysis method.
nucleation and crystal growth of the nanocrystals, but rarely with successful device performance obtained from the synthesized nanocrystals. Generally, high quality CZTS nanocrystals with controllable phase, solubility, and composition, together with a proper selenization process for the as-deposited nanocrystal film, allow the annealed CZTS film to translate into an excellent absorber layer for photovoltaic applications. The controllable synthesis and selenization will be discussed in Section 3.4 and 4.3, respectively.

3.2 CZTSe nanocrystals

The synthesis of CZTSe nanocrystals can also be carried out by introducing selenium sources to precipitate from the metallic precursors in coordinating solvents. The resulting quaternary compound semiconductors possess a kesterite crystal structure of high phase purity, as well as controllable composition. Typically, the metal salts used for synthesizing CZTSe nanocrystals are chlorides, acetates, and acetylacetonates, similar to those used in producing CZTS nanocrystals. The solvents, however, show some significant differences, as selenium based NCs synthesis usually involves the preparation of soluble Se precursors in alkylphosphines, such as trioctylphosphine (TOP) and tributylphosphine.

A phosphine-free route for synthesizing high-quality CZTSe NCs (Fig. 4c) in organic solvents has been achieved using the fact that selenium powder can be first reduced by DT in the presence of OM to generate a soluble alkylammonium selenide at room temperature, bypassing the conventional requirement of extended heating to dissolve selenium powder. This adaptive method generates CZTSe NCs with small size, excellent monodispersity, and strong absorbance in the visible region. Currently, using CZTSe nanocrystals, the demonstrated PCE is less than 5%, significantly lower than the performance of devices based on CZTS nanocrystals. The possible reason could be ascribed to less effective selenization for the CZTSe nanocrystals, producing an inferior grain structure for the CZTSe film. The selenization for CZTS nanocrystals, with Se replacing S, leads to an enlarged lattice parameter and a well-defined grain structure. Nevertheless, CZTSe nanocrystals become another good candidate for obtaining precise control of the final CZTSe films with tunable band gaps, or even gradient band gaps, to further optimize the device performance.

3.3 CZTGeS nanocrystals

CZTGeS nanocrystals are synthesized by the same procedure as reported for CZTS by partially substituting germanium for tin. The most commonly used Ge precursor is germanium chloride, with copper acetylacetonate, zinc acetylacetonate hydrate, and tin bis(acetylacetonate) dibromide, with sulfur dissolved in oleylamine completing the reaction system. The as-synthesized CZTGeS nanocrystals have been used to fabricate CZTGeSSe thin films, and have produced impressive device performance values as high as 8.4%. More information about the band gap tunability provided by germanium and its effects on device performance will be discussed in Section 4.5.

3.4 Synthetic chemistry for size, shape, composition, and phase control

CZTS and CZTSe nanocrystals are selected as the typical examples to explain the general synthetic chemistry for size, shape, composition and phase control. Other analogous nanocrystals, e.g. CZTSSe nanocrystals and CZTGeS nanocrystals, share a similar reaction mechanism.
3.4.1 Size control. To construct high performance CZTSSe films, the average particle size for CZTS nanocrystals should preferably be kept under a few tens of nanometers, to achieve good solubility in the desired solvent. Through adjusting the reactivity of precursors and the coordinating ability of the surfactants and solvent, the average particle size for the as-prepared CZTS or CZTSe nanocrystals falls in the range of 10 to 40 nm in most successful cases. Longer reaction durations, and slower reaction rates of chalcogenide precursors, will produce nanocrystals with larger particle sizes. In some cases, much smaller CZTS nanocrystals with diameters between 2 and 7 nm (Fig. 5) can be controllably achieved by an accelerated decomposition reaction. Generally, it is beneficial to carefully control the size of semiconducting nanoparticles in order to alter their optical properties due to the quantum confinement. However, since these devices are based on annealed CZTSSe films after combining the nanoparticles into large grains, the effects of quantum confinement become negligible on the final device. While, very narrow size distribution of the initial CZTS nanoparticle is necessary to obtain a close compact film, since the attractions between semiconductor nanoparticles are weak. Further study on the size effect could be carried out by fixing other parameters, e.g., the composition, the selenization process, to demonstrate their effects on device performance, or the nanoparticles themselves could be used to construct other low temperature optoelectronic devices. It is possible that the particle size, which affects the specific surface area of the nanocrystals, can influence the quantity of surface ligands present in as-deposited films, which will then exert further influence on grain growth and device performance. The tradeoff between impurities left behind by decomposing surface ligand and the need for high dispersibility in the precursor inks is an ongoing dilemma in nanoparticle-based solar cell fabrication.

3.4.2 Compositional control. The narrow phase stability and volatile nature of some of its elemental constituents associated at high temperatures make compositional control of the metal cations extremely important for high performance CZTSSe films. The chemical composition of the obtained CZTS or CZTSe NCs can be tuned by changing the reaction conditions, including temperature, type of precursor, and reagent concentration. Many of the compositional difficulties arise from Cu₃S precipitating first due to its small solubility product of $2.5 \times 10^{-48}$, followed by the chemical transformation of Cu₃S to CZTS facilitated based on the relatively high atomic diffusivity of copper. Among the binary chalcogenides, Cu₅S₃, ZnS, and SnS₂, ZnS shows the largest solubility product, and so becomes the last constituent to be incorporated into the CZTS phase. This is reflected by a tendency toward reduced zinc content in the final composition of nanocrystals, compared to the initial composition of the precursor solution. Thus, the successful balancing of the reactivity of the metal precursors and the chalcogenide source, and the reaction conditions in terms of time and temperature, is thought to be the key to the successful development of synthetic schemes capable of producing quaternary compounds with highly predictable composition.

3.4.3 Morphology control. The morphology of the as-synthesized CZTS or CZTSe NCs is largely dependent on the choice of surfactants and reaction conditions. Different surfactants are able to selectively bind on particular facets, allowing for anisotropic growth in certain directions, e.g. dodecanethiol and tert-dodecyl mercaptan binding on facets other than (002) to produce CZTS nanorods. Additionally, it has been reported that changes in reaction time can lead to different forms of reaction products varying from kinetically favorable to thermodynamically favorable, e.g. from sphere-like, to rhombus-like, and then to rice-like, as the reaction time is increased from 30 min to 1 h and to 2 h (Fig. 5). Considering the high temperature annealing process that takes place during device fabrication, morphology control in CZTS nanoparticle synthesis has more impact for its role to form CZTS nanocrystals that are ideal building blocks for film formation, rather than directly affecting the electrical properties of the final materials.

3.4.4 Phase control. Due to the rather narrow phase window, it is crucial to synthesize CZTS nanocrystals with a pure kesterite phase with effectively no trace of detrimental secondary phases, e.g., Cu₅SnS₃, and ZnS. In colloidal nanocrystal synthesis, the type of capping ligands and the reactivity of the precursors are known to strongly influence the crystallographic phase of the nanocrystals. Because kesterite is the thermodynamically stable phase, precursors with relatively low reactivity and solvents or surfactants with weaker coordination toward metal cations will drive the reaction in its direction. For example, OM is found to be effective in promoting the formation of the kesterite CZTS structure, while alkanethiols are pivotal in producing wurzite CZTS, because of the stronger coordination between the metal cations and thiol groups, adjusting the chemical environment and ultimately encouraging the formation of hexagonal structures. Currently, all demonstrated working devices are based on kesterite CZTS nanocrystals, and it is predicted that they will
continue to exhibit much higher device performances than those based on wurtzite nanocrystals. However, since the metastable wurtzite structure can be transformed into the more stable kesterite structure after high temperature annealing, the wurtzite nanocrystals still could represent a possible route toward ink fabrication if they prove to be easier to synthesize or formulate into inks.

3.5 CZTSSe films from binary and ternary nanocrystals

Another facile fabrication method for CZTSSe films is starting from binary and ternary metal sulfide nanoparticles, including copper tin sulfide (CTS), ZnS, SnS2, and Cu2−xSx, which are synthesized by reacting metal salts with sulfur in OM and TOPO. The as-synthesized binary and ternary nanoparticles are then dispersed and combined in solution to yield completed inks with the desired particular metal composition. The resulting ink blends can then be cast into thin films by standard methods like spin-coating to yield smooth, dense CZTS precursor coatings, which are subsequently converted into CZTS or CZTSSe in a thermal processing step. The CZTSSe phase can be obtained either through the reaction between a mixture of CTS and ZnS nanoparticles and a small amount of SnS nanoparticles, or the reaction among a simple mixture of three binary nanoparticles. This indicates that although the preformed nanocrystals are crystalline, each constituent in the nanocrystals can diffuse effectively within the film to reach a thermodynamic stable phase. This approach reduces the problem of composition control to a simple mixing of precursors in known proportions. Starting from the binary and ternary nanocrystals, the annealed device shows PCE values as high as 8.5%, apparently indicating that successful diffusion and phase formation occurred during the high temperature annealing step. The annealed film was reported to exhibit lateral and vertical non-uniformity in terms of the composition, which affects the device performance, suggesting that a more optimized way to control film composition is urgently needed.

3.6 CZTSSe phases based on colloidal nanocrystals and MCC ligands

Starting with colloidal Cu2−xSx NCs and ZnS NCs, both capped with long-chain alkylamine ligands, and treating them with dissolved (NH4)2SnS6 metal chalcogenide complexes (MCCs), a soluble precursor for the solution deposition of CZTSSe films has been reported. Both NCs easily exchange their original capping ligands for SnS42− ions and form stable colloidal solutions in amine-containing solvents, such as formamide or N-methylformamide. The solutions containing stoichiometric amounts of SnS42−-capped Cu2−xSx NCs and SnS64−-capped ZnS NCs were combined together without any losses of colloidal stability, deposited, and annealed at 500 °C in an inert atmosphere. Annealing for 20 min was sufficient to obtain highly crystalline CZTSSe films. In addition, the CZTSSe film obtained by this process contains less carbon residue after the high temperature annealing step, as inorganic ligands have been substituted for the usual long-chain alkylamine ligands, which will likely be beneficial to the performance of resulting devices. Similarly, a facile preparation approach based on Cu2−xSx NCs and Zn/Sn ligands has been developed with a simple, neat reaction pathway to form CZTSSe films. The reaction between colloidal nanocrystals and MCC ligands to form the CZTSSe phase is based on the effective diffusion of each constituent from both the core nanoparticles and the ligand shells. Whether this approach provides a favorable reaction pathway is unclear in the current stage. Until now, no photovoltaic devices have been made based on this approach; however, this method can be potentially used to address the issues of undesirable carbon residues arising from the decomposition of surface ligands on colloidal nanocrystals (Fig. 6).

3.7 Hydrophilic synthesis methods

The preceding discussion summarized the colloidal thermolysis growth method as a versatile and powerful tool to prepare CZTS nanocrystals and films with a variety of structural properties. It
provides as-synthesized nanocrystals with controllable phase, size, shape, and composition, as well as good dispersibility in nonpolar solvents. However, thermolysis is not the only available method to synthesize CZTS nanocrystals. Some other successful examples are based on solvothermal methods. A modified solvothermal method was used to synthesize CZTS with the precursors, SnCl2·2H2O, CuCl2·2H2O, and ZnSO4·7H2O, in an ethylene glycol solution containing PVP and Na2S·9H2O at 180 °C for 12 h. The mechanism for synthesizing CZTS NCs is based on the reaction that occurred between the metal precursors and the sulfur source in desired solvent, while PVP mainly acts as capping ligands on nanocrystals. As a result of the presence of the PVP and/or ethylene glycol ligands, the CZTS NCs are hydrophilic and can be readily dispersed in ethanol and water with a high stability (Fig. 7a).7 Besides particles, some novel structures for CZTSSe can be achieved by the solvothermal method, e.g., hierarchical CZTS particles, CZTSSe nanosheets (Fig. 7c), CZTS and CZTSe nanowires (Fig. 7d), and CZTSSe–CZTS core–shell nanocable bundles.61 So far, CZTS or CZTSe nanostructures prepared from the solvothermal method have only occasionally been reported with good device performance, probably associated with difficulties related to film formation. But some novel structures, e.g., nanowires, are promising for the carrier transport and collection, and may prove beneficial for low temperature devices, or devices based on single nanowires.

In summary, the thermolysis method is based on burst nucleation and selective growth, in which the collective reactivity among metal precursors, chalcogen source, and surfactant has a strong impact on the properties of the as-prepared nanocrystals. Although not optimal for high quality particle synthesis, solvothermal growth and other processes using high temperature, high pressure, or templates are able to generate a larger variety of metastable structures. Additionally, methods other than thermolysis do not rely on the presence of long chain ligands, which can reduce the amount of undesirable carbon residue in the sintered film, but tend to suffer from inferior solubility prior to film formation. Compared with the thermolysis method, which produces nanocrystals with finely controlled size, shape, composition, phase, and dispersibility, there is still plenty of room for further improvement in CZTS nanocrystals synthesized by other approaches to continue to advance the available methods for CZTSSe film formation and resulting device performance.

4 Absorber formation and device performance

CZTSSe solar cells made by the nanocrystal selenization approach have to date attained cell efficiency just near 10%. Here, we offer an overview and evaluation of the best performance solar cell achieved by this technique, and observe its notable properties as they appear in the current–voltage characteristics, external quantum efficiency (EQE) spectra, and other optical or electrical characterization results for both films and devices. An introduction to the typical processing steps of absorber film formation and device fabrication is provided, and afterwards we discuss a number of remaining challenges and possible future directions. These issues generally center around selenization conditions, grain morphology, elemental composition, and band gap tuning. Finally, we draw the attention to approaches based on non-sintered CZTS nanocrystal thin films, which cannot match the performance of large-grain CZTSSe at their present stage but show some potential for improvement if a way is found to better passivate the large surface area present in nanocrystalline films.

4.1 Methodology of absorber formation and device fabrication

Typical absorber deposition consists of a two-step process using the finished nanocrystals. This two-step process includes a low-temperature film deposition step followed by a separate high-temperature thermal treatment. The nanocrystal coatings are accomplished by either repeating spin coating or doctor blading to achieve 1 to 2 μm of film thickness. Soft baking around 300 °C was done in between each coating. The films were then annealed at 500 °C to 560 °C for durations longer than 20 min within an elemental selenium atmosphere, a step known as selenization. The device structure typically follows the historical and empirical route for high performance CIGS devices, with Mo/CZTS/CdS/ZnO/ITO as the typical structure, as shown in Fig. 8.

4.2 Cell performance and evaluation

The performance of the CZTSSe solar cells by the nanocrystal approach is progressing at the initial pace of several other material systems. Multiple techniques have achieved conversion efficiency near 10%, but are limited by a deficiency in open circuit voltage ($V_{oc}$). Losses in fill factor (FF) and short-circuit current ($J_{sc}$) are secondary to $V_{oc}$ but still offer plenty of room...
for improving. Table 1 lists the PCE and important current-voltage (J-V) parameters ($V_{oc}$, FF, and $J_{sc}$), and the energy bandgaps estimated from the external quantum efficiency (EQE) spectra of the latest CZTSSe cells by nanocrystal selenization, and also the parameters of the champion cell of all the reported kesterite cells today by a hydrazine-based coating process. The original J-V curves of the 8.5% nanocrystal cells by DuPont\textsuperscript{18} and that of the 11.1% champion cell made by IBM\textsuperscript{13} are also provided in Fig. 9a and b, respectively. Their quantum efficiency spectra (QE) are shown in Fig. 9c and d, respectively.

4.2.1 $V_{oc}$ and recombination loss. The limitation of open circuit voltage ($V_{oc}$) is one of the most important issues that CZTSe devices are currently facing, regardless of their fabrication method. The temperature-dependent $V_{oc}$ is given as

$$V_{oc} = \frac{E_a}{q} - \frac{n k T}{q} \ln \left( \frac{J_0}{J_L} \right),$$

where $k$ represents the Boltzmann constant, $q$ is the electronic charge, $n$ is the diode ideality factor, and $J_L$ and $J_0$ represent the photogenerated current density and saturation current density, respectively. The $V_{oc}$ versus $T$ plot is in theory a straight line, and $E_a$, the activation energy of the dominant recombination mechanism, can be extrapolated at $T = 0$ K.\textsuperscript{62} A relatively high quality chalcopyrite solar cell generally shows $V_{oc}$ values 500 mV lower than its band gap\textsuperscript{62} which makes the extracted activation energy equal to $E_g/q$, indicating that the main recombination mechanism is band-to-band. However, all of the cells shown in Table 1 and many other reported good kesterite devices\textsuperscript{13,63} show voltage deficits of more than 600 mV, which reveals the presence of other recombination mechanisms involving deep traps within the band gap. Several other relevant measurements have also been done to confirm the undesirably strong recombination rates in these cells. (1) Time-resolved photoluminescence (TRPL) shows that minority carrier lifetimes are 1 to 2 orders of magnitude smaller than that of a high-performance CIGS cell. Fig. 10 shows the PL decay of a 6% efficient CZTSSe cell made by the nanocrystal approach [Y. Yang, unpublished] and an 11% hydrazine-processed CZTSSe sample,\textsuperscript{13} respectively. The carrier lifetime of the CZTSSe devices are demonstrably short for both cells, falling in the range of a few nanoseconds. (2) The loss of photocurrent due to recombination can be observed from the fast decay of the EQE spectrum toward longer wavelengths, where photons are mainly absorbed in a deeper position within the absorber and thus have less chance to be collected because of the short minority carrier diffusion length, expected to be less than 200 nm based on the minority carrier lifetime measured from TRPL (assuming that the absorber exhibits a superior electron mobility of $\sim$5 cm$^2$ V$^{-1}$ s$^{-1}$). The EQE spectra of the 8.5% cell made by the nanocrystal approach and the 11.1% champion cell are shown in Fig. 9c and d, the difference in shape of the two spectra is extremely small, indicating that the diffusion length in the bulk of the two absorber layers is comparable.

<table>
<thead>
<tr>
<th>Absorber</th>
<th>Research group</th>
<th>PCE</th>
<th>$V_{oc}$</th>
<th>$J_{sc}$</th>
<th>FF</th>
<th>$E_g$</th>
<th>$E_g/q - V_{oc}$</th>
<th>AR</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nanocystal-annealed cell</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$_2$ZnSn(S,Se)$_4$ (ref. 18)</td>
<td>DuPont</td>
<td>8.5</td>
<td>451</td>
<td>28.9</td>
<td>64.9</td>
<td>1.1</td>
<td>649</td>
<td>X</td>
</tr>
<tr>
<td>Cu$_2$ZnSn(S,Se)$_4$ (ref. 17)</td>
<td>Purdue U</td>
<td>7.2</td>
<td>430</td>
<td>31.2</td>
<td>53.9</td>
<td>1.1</td>
<td>670</td>
<td>X</td>
</tr>
<tr>
<td>Cu$<em>2$Zn(Sn$</em>{0.75}$Ge$_{0.25}$)(S,Se)$_4$ (ref. 49)</td>
<td>Purdue U</td>
<td>8.38</td>
<td>464</td>
<td>29.4</td>
<td>64.04</td>
<td>1.09</td>
<td>626</td>
<td>X</td>
</tr>
<tr>
<td>Cu$<em>2$Zn(Sn$</em>{0.30}$,Ge$_{0.70}$)(S,Se)$_4$ (ref. 46)</td>
<td>Purdue U</td>
<td>6.8</td>
<td>640</td>
<td>21.5</td>
<td>49</td>
<td>1.4</td>
<td>760</td>
<td>X</td>
</tr>
<tr>
<td>Cu$_2$ZnSn(S,Se)$_4$, flexible$^*$</td>
<td>Solexant</td>
<td>9.85</td>
<td>457</td>
<td>32.62</td>
<td>66.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Champion cell of all reported kesterite cells</strong></td>
<td>IBM</td>
<td>11.1</td>
<td>460</td>
<td>34.5</td>
<td>69.8</td>
<td>1.13</td>
<td>670</td>
<td>O</td>
</tr>
</tbody>
</table>

$^*$ Sn/Ge ratios shown are composition of as-synthesized nanocrystals instead of that of the selenized thin film.
4.2.2 FF and parasitic resistance. Second to recombination losses, parasitic resistance is also a concern for CZTSSe solar cells made from the nanocrystal approach. These cells have a slight but noticeable deficiency in FF compared to the champion cell, which is mainly affected by a higher series resistance. Series resistance as low as 0.2 ohm × cm² is achievable in CZTSe devices made by co-evaporation and therefore we believe that high series resistance is not a problem intrinsic to the material, and can be solved by careful tailoring of the fabrication process. Pronounced cross-over behavior at less than 10 mA cm⁻² between the light and the dark curves, as shown in Fig. 9a, could be an indication of severe barriers to current transport between device layers, while for the IBM cell shown in Fig. 9b this cross-over does not occur until 54 mA cm⁻² forward current. However, such cross-over behavior is not evident in the J-V characteristic of all the reported cells made by nanocrystal approaches, indicating that further optimization may be able to remove such issues from nanocrystal-based devices altogether.

4.2.3 Short circuit current density. Losses in short-circuit current density (Jsc) are modest compared to the loss of Voc, but definitely offer room to improvement. Absorber materials made by the CZTS nanocrystal approach have no intrinsic difficulties in optical absorption judging from their high EQE values, which approach 95% at their maximum point even without an anti-reflection layer. Nevertheless, Jsc can be further improved if the loss in EQE at longer wavelengths range can be reduced. As mentioned, carrier recombination is responsible for the loss of electron–hole pairs generated deep inside the film where long wavelength photons are mainly absorbed. Improving the collection of long wavelength light would be a useful addition to the already large photocurrents generated in high quality CZTSSe absorbers.

In brief, the improvement of the CZTSSe device performance by the nanocrystal approach should be majorly focused on the reduction of surface/bulk recombination, the removal of additional series resistance, and lastly, the enhancement of absorption of long-wavelength photons.

4.3 Selenization/sulfurization, film morphology, and device performance

High-temperature thermal annealing processes are nearly always employed for the as fabricated nanocrystal films, and remarkable grain growth is required to avoid excessive recombination and carrier scattering from the boundaries between nanocrystals. Based on previous experience with CIGS, only films with micron sized grains have a chance to produce cells with high power conversion efficiencies. Current progress in CZTS nanocrystal based solar cells has demonstrated that without a grain-growing thermal annealing process, solar cells are generally unable to reach 1% efficiency. Therefore, even though the crystal structure of kesterite has been formed in the as-deposited films, thermal annealing cannot be omitted due to its importance in ensuring grain growth.

Even though the nanocrystals already contain a significant amount of chalcogen (sulfur in most cases), the thermal annealing process of nanocrystal films still requires the presence of chalcogen vapor, generally at pressures near one atmosphere. Under high vacuum conditions, the CZTS phase decomposes at temperatures above 550 °C. The products of the decomposition reaction include a number of volatile phases, including SnS and elemental sulfur. The decomposition rate largely varies depending on the temperature, total pressure of the chamber, and the partial pressure of the volatile products. To prevent the loss of CZTS phase and the formation of undesired phases, in the recent studies, an atmospheric base pressure and a chalcogen source have been applied in the thermal annealing process. While supplying sulfur (sulfurization) or selenium (selenization) are both reasonable options to prevent the decomposition of CZTS and CZTSe, to date successful devices are all made via selenization processes, which replace over 90% of S by Se according to Auger Emission Spectroscopy (AES). The main differences between sulfurization and selenization lie in their ability to initiate and propagate grain growth.

4.3.1 Selenization. The selenization setup usually makes use of a graphite box holding as-deposited nanoparticle films and elemental selenium, which is placed into a quartz tube furnace with a slow continuous inert gas flow. The annealing temperature is typically reported between 500 °C and 560 °C for more than 20 minutes.

Selenization of the nanocrystal film generally produces bilayer structures, with a large-grained layer on top and a fine-grained layer on the bottom and, in some cases, another large-grain layer at the bottom forming a tri-layer structure. The SEM image shown in Fig. 11a is one of the examples of double-layer
structure and is fairly similar to data reported elsewhere.\textsuperscript{37-49} Fig. 11b (ref. 32) is an example of a tri-layer structure. All these films produce device efficiencies in the range of 7–10%. These studies also indicate that the large-grain layer is the CZTSSe phase, and the fine-grain layer is a mixture of CZTSSe and binary chalcogenide nanocrystals embedded in a matrix of carbon residue.\textsuperscript{18} These features of the final films appear to be distinctive from those made by other processes. They reveal that during sintering of a nanocrystal film, a recrystallization process initiates on the surface of the film and in some cases on the molybdenum interface as well where the interfacial energy is the greatest and the thermal activation barrier of recrystallization is the smallest. These recrystallization fronts are able to produce grains one or more microns in diameter, while the simple ripening of nanocrystals that are far from each interface proceeds much slower.

The involvement of carbon, left behind by the nanocrystal ligands, is suspected as the cause of the unique morphology exhibited by the sintered nanoparticle films. A similar morphology has also been observed in a different ink-based process for CIGS solar cell fabrication (Fig. 11c),\textsuperscript{46} in which a significant amount of carbon in the form of ethylcellulose was added to improve the viscosity and coating behavior of a precursor paste. Metal elements and chalcogens precipitate out from the mixture of carbon, chalcogen, and metal ions and the CIGS grains only nucleate on the surface of the film. In carbon-free CZTSSe films fabricated from hydrazine-based inks,\textsuperscript{67,11} no fine-grained layer is observed, as shown in Fig. 11d.\textsuperscript{41} Grains are stacked on top of each other, which indicates that in the beginning of the thermal process nucleation takes place throughout the bulk of the film.

The unique layered structure of annealed nanoparticle films can be expected to exert a variety of effects on the performance of the resulting devices. The large CZTSSe grains are arranged in a single monolayer, which means that CZTSSe grain boundaries lying across the direction of carrier motion have been completely avoided. On the other hand, the fine grain layer may contribute to device series resistance, and is completely inactive in current generation. Below the tri-layer cross-sectional SEM image in Fig. 11 is a cross-sectional EBIC map for the same area (a 9% CZTSSe nanocrystal sintering device\textsuperscript{42}). As indicated in the map, only the top large grains produce signal, which means that only the top large grains effectively contribute to the photoresponse of the device under illumination. The elimination of the fine-grain layer and the thickening of the effective large-grain layer should lead to an improvement in device performance by reducing the series resistance and also enhancing the absorption of long wavelength photons. If the removal of carbon from the nanocrystal inks is demonstrated to help with this effect, major changes may need to be made earlier in the fabrication process either as the ink is prepared or during the nanocrystal synthesis itself.

Besides the grain growth of the kesterite layer, the reaction between Mo and chalcogen vapor also affects the device structure and resulting performance. Due to the robust reaction between Mo and Se, a layer of MoSe\textsubscript{2} is generated as thick as several hundred nanometers in between Mo and the CZTSSe layer. As the thickness of the molybdenum electrode is reduced, the series resistance of the device increases, especially when larger-area cells are fabricated. It has been documented that optimizing the working pressure and sputtering power as well as introducing a small amount of oxygen during molybdenum deposition can reduce the thickness of the growing MoSe\textsubscript{2} layer.\textsuperscript{46}

### 4.3.2 Sulfurization

The sulfurization of CZTS nanocrystal films has encountered difficulties in achieving grain sizes anywhere near those achieved by selenization, and therefore has not demonstrated particularly successful device performances. Lu \textit{et al.} annealed CZTS nanocrystal films in an elemental sulfur atmosphere at 500 °C but the grain size remained tens of nanometers and the device efficiency was less than 1%.\textsuperscript{46} Tian \textit{et al.} reported annealing of the CZTS nanocrystal film with elemental sulfur at the same temperature while the nanocrystals were capped by hydrophilic ligands. Ethylene glycol, which can be used as a hydrophilic ligand, has only two carbon atoms for each molecule and therefore would contribute much less carbon compared to the oleylamine ligands used in most other works. In this case, CZTS grains grow beyond several hundred nanometers but still appear observably smaller than the selenized films shown in Fig. 11. The device efficiency was 1.94%.\textsuperscript{37} Since sulfur has a lower melting point than selenium, it is reasonable to assume that supplying sulfur vapor is not more difficult than supplying selenium vapor. The difference between the effects of sulfurization and selenization in terms of grain growth is at present not fully understood, but it is clear that selenization is the more favorable process at this point. In addition, other processes which do not have problems in achieving large sulfide grains also indicate some difficulties in achieving sulfide devices as good as selenide devices, especially seen in the loss of $V_{oc}$. Reports on several devices fabricated by the hydrazine-based...
process, co-evaporation process, and sputtering process can be found in a previous review paper.\textsuperscript{30} The pure CZTS devices generally have significantly larger $E_{g}/J_{sc}$ compared to the CZTSSe devices. The reason could relate to defect chemistry but remains unclear in the present stage.

4.4 Elemental composition and its effect on the device

It is generally true for all the kesterite solar cells fabricated by different approaches that device performance strongly depends on absorber stoichiometry, which determines the defect species and population and whether or not detrimental secondary phases exist. The composition of the best devices made by the nanocrystal approach\textsuperscript{27} is Cu-poor and Zn-rich relative to the stoichiometric composition of the CZTS phase, which matches with the optimized compositions found by other approaches,\textsuperscript{16,18} of Cu(\text{Zn + Sn}) \approx 0.9 and Zn/Sn \approx 1.25. The stoichiometric composition yields devices with significantly lower $V_{oc}$, $J_{sc}$, and FF.\textsuperscript{18} The most important factor determining the composition is intuitively the composition of the as-synthesized nanocrystals. However, the selenization process often changes the bulk composition and produces a non-uniform composition distribution along the vertical direction, and therefore the optimized stoichiometry of the as-synthesized nanocrystals should be adjusted accordingly to reach a targeted post-selenization stoichiometry.

The loss of Sn due to the evaporation of the binary phases SnS and SnSe\textsuperscript{ss} has been reported as the major change in film composition during selenization.\textsuperscript{27} In addition, when Ge is incorporated, the loss of Ge is higher than the loss of Sn. (More discussion on Ge loss and the resulting reduction in bandgap can be found in Section 4.5.) Generally, the change in bulk composition is mild because the decomposition rate is restricted by the atmospheric pressure and significant amount of selenium vapor present during the annealing process. A more noticeable phenomenon is the production of a vertically non-uniform distribution of metal elements as a result of the complex bi-layer or tri-layer morphology. The Auger Emission Spectroscopy (AES) composition depth profile reported by DuPont\textsuperscript{28} is shown in Fig. 12. A few typical observations for films formed in this manner: (1) the atomic percentage of each element is not flat even within the individual large-grain or fine-grain layers. (2) The metal compositions within the large-grain layer are different from those within the fine-grain layer. The percentage of Cu in the Cu-poor fine-grain layer is less than half of that in the large-grain layer, while the percentage of Zn is only slightly lower, and the percentage of Sn is actually higher. (3) At the bottom of the absorber, where Mo(S,Se)\textsubscript{2} is observed, the percentage of Cu is almost as high as in the large-grain layer. Variation of composition is not surprising since the constitution of the thermodynamic system is complex throughout the vapor/large-grain CZTSSe/nano-sized CZTSSe/carbon/MoSe\textsubscript{2} structure during selenization.

So far, there are no studies showing how to adjust vertical elemental distribution or how it affects the device performance. It is reasonable to assume that the metal ratios in the top large-grain layer are more critical than the bulk metal ratios, also taking into account the large quantity of metals in the carbon-rich layer and the thick Mo(S,Se)\textsubscript{2} layer. Further optimization of the composition of the front large grains or other details of elemental distribution may improve the $V_{oc}$ by reducing defect density and homogenizing the vertical distribution of the defects. Since the commonly used energy dispersive spectroscopy (EDS) or X-ray fluorescence (XRF) can only give the bulk metal ratios of the large-grain layer, information relevant to device performance is missed. Advanced characterization tools such as AES or X-ray photoelectron spectroscopy (XPS) with depth profiling should be therefore continuously involved in the optimization process.

4.5 Band-gap tunability and the effect on device performance

An optimized absorber band gap makes it possible to achieve a balance between the output current and voltage of the resulting solar cells. Absorbers with low band gaps create higher radiative recombination loss resulting in a lower $V_{oc}$. An overly large band gap is also not beneficial since it exhibits narrow absorption behavior that fails to utilize longer wavelength photons. The model of the Shockley–Queisser detailed balance limitation indicates that an optimized band gap is located in the range 1.15–1.35 eV.\textsuperscript{70} Kesterite compounds with a configuration of I_2–II–IV–V_4 have naturally suitable and tunable bandgaps. A summary of the evolution of the electronic structure of multinary chalcogenide semiconductors can be found in a previous publication.\textsuperscript{71} In brief, the band gaps of I–III–VI_3 and I_2–II–IV–V_4 compounds are narrower than those in II–VI and are in a more appropriate position for solar cell applications. The bandgaps of I–III–VI_3 and I_2–II–IV–V_4 compounds can be further fine-tuned by common group ion substitution. In the CIGS system, common group ion substitution between S and Se and between Ga and In is a well-known strategy for optimizing the material’s band gap. This approach has also been adapted by the kesterite system. Cu_2ZnSnSe_4, Cu_2ZnSnS_4, Cu_2ZnGeSe_4, and Cu_2ZnGeS_4 have increasing band gaps of 0.94 eV,\textsuperscript{73} 1.45 eV,\textsuperscript{73} 1.51 eV,\textsuperscript{73} and 2.27 eV,\textsuperscript{71} respectively. The optimized band gap can be obtained by alloying these kesterite compounds. As all studies of kesterite solar cells to date are unsatisfactory by the low $V_{oc}$, we are eager to
search for ways to decrease recombination and increase the output voltage. It is equally if not more important to note that introducing more elements will inevitably also introduce more species of antisites and vacancies, some of which may act as recombination centers. In other words, kesterite films with different S/Se and/or Sn/Ge ratios not only exhibit different absorption band gaps but also different of $V_{oc}$ deficits. Without knowing the exact origin of the $V_{oc}$ deficit, current research efforts are exploring these alloyed compounds in order to acquire a better understanding of the observed device performance values.

4.5.1 S/(S + Se) tuning. Varying the S/(S + Se) ratio has been investigated through a variety of vacuum$^{75}$ and non-vacuum approaches.$^{16,67,76}$ By hydrazine-based processing, films with S/(S + Se) values of 0.03 and 0.4 have both yielded device efficiencies over 10%; by thermal evaporation, films with 0.34 and 1.0 of S/(S + Se) have also yielded over 7%. However, as described in Section 4.3, sulfurization experiences difficulty in enhancing grain growth from nanocrystals and the device efficiencies remain lower than those of selenium-rich devices.$^{68,77}$ Another possible strategy is to supply less selenium vapor while annealing sulfide nanocrystals to prevent the total replacement of sulfur by selenium. However, the required minimum selenium amount to initiate grain growing is already enough to replace most of the sulfur atoms, which explains why no devices reported today are made by slightly selenized CZTS nanocrystals. In brief, the nanocrystal approach does not currently offer a knob to freely adjust the S/Se ratio by varying the amount of selenium supply in the selenization process.

4.5.2 Ge/(Sn + Ge) tuning. Partial substitution of Sn by Ge is more frequently reported for the nanocrystal approach, and was first demonstrated with nanocrystals$^{46,49}$ prior to its successful incorporation into hydrazine-based processing.$^{77}$ Besides concerns over grain growth, other benefits for using Ge/Sn tuning rather than sulfur/selenium tuning include the following: (1) the compositions of Ge and Sn can be fixed in the as-deposited film and they change relatively little throughout the selenization process compared to S and Se. (2) Since Sn is a multivalent element, the oxidation state is potentially changeable during device operation and can act as a recombination center.$^{77}$ (3) Adapting experience from CIGS solar cells,$^{78,79}$ substituting Sn by Ge allows for the modulation of the Conduction Band Minimum (CBM) without moving the Valence Band Maximum (VBM) significantly,$^{71}$ which allows for the creation of a back surface field and that can beneficially affect device performance.

In practice, Ge is incorporated into CZTS as the nanocrystals are synthesized, but the increased bandgap does not fully transfer to the completed devices. Fig. 13 displays the results of several previous reports.$^{17,18,49,80}$ Ge/(Sn + Ge) ratios employed in nanocrystal synthesis and the band gaps of their resulting devices derived from EQE spectra$^{77}$ are plotted. The estimated bandgap (the dashed line) is calculated by linear interpolation assuming the S/(S + Se) = 0.33. (0.33 is chosen to match the data point of Ge/(Sn + Ge) = 0. The S/(S + Se) ratios of these samples are often not reported accurately in the literature.) A deviation from the bandgap estimated by EQE to that estimated by linear interpolation is evident for every data point with Ge/(Sn + Ge) = >0. This leaves one very likely result: the actual ratio of Ge/(Sn + Ge) in the selenized absorber is lower than that of the nanocrystal because the loss in Ge during selenization is higher than that of Sn.

In terms of current-voltage ($J–V$) performance, device efficiencies of 8.3% have been obtained by selenizing nanocrystals with Ge/(Sn + Ge) = 0.25 (ref. 49) and 6.8% by selenizing nanocrystals with Ge/(Sn + Ge) = 0.7 (ref. 46) compared to a previously reported device with 7.2% efficiency fabricated without any germanium.$^{77}$ The 0.70 Ge/(Sn + Ge) device does add 210 mV on the $V_{oc}$, bringing the $V_{oc}$ to 640 mV, which is the highest among all devices made by the nanocrystal approach (listed in Table 1). Even though the $V_{oc}$ is raised, considering the bandgap increment of 300 meV, the $V_{oc}$ deficit is in fact increased by 90 mV.$^{80}$ The larger $V_{oc}$ deficit implies increasingly active defect levels in the germanium-rich films. Capacitance-voltage (C–V) measurements at room temperature consistently suggest an increasing number of deep levels, interfacial defects, and free carrier concentration with increasing Ge/(Sn + Ge) ratio.$^{81}$

The increase of $V_{oc}$ deficit when the band gap is enlarged is not unique to this work. It has been observed in hydrazine-processed Cu$_2$Zn(Ge,Sn)(S,Se)$_4$.$^{77}$ and even earlier was experienced in studies trying to increase the Ga content in CIGS solar cells.$^{82}$ In CIGS studies, by raising the processing temperature, the $E_g/q – V_{oc}$ value has been successfully reduced to about 560 mV as for band gap values around 1.4 eV. An improvement of $V_{oc}$ in Cu$_2$Zn(Ge,Sn)(S,Se)$_4$ devices is also possible at higher temperatures, but is expected to present more challenges during implementation due to the large number of potentially volatile elements involved. Other reported problems in Ge-incorporated devices are the loss in carrier collection from longer wavelengths and the loss in FF.$^{80,81}$

4.6 The fabrication of low temperature CZTS and hybrid CZTS nanoparticle-based devices

As mentioned, without high-temperature selenization, the CZTS nanocrystal films have not demonstrated acceptably high cell
performance values. The large surface area of the nanoparticles, which serves as deep recombination centers and scattering sites for carriers, is the most glaring difference when comparing the two approaches. However, if a way to passivate the crystal surface can be found, the low-temperature feature of this process becomes attractive for many reasons.

The formation of the kesterite phase typically demands thermal processing temperatures higher than 450 °C by solid-state reaction depending on the choice of reactants. Synthesizing the CZTS phase in solution can be precisely controlled at temperatures slightly above 200 °C. The low temperature process brings in many advantages for the further development and manufacturing concerns. First, the high energy input during device production is significantly lower and the energy payback time for these devices is substantially shorter. Second, low temperature processing provides more opportunities for using flexible and light-weight plastic substrates and metallic foils, which means lower module manufacturing and installation cost. Metal foils have been utilized in the fabrication of CIS solar cells in high-temperature processes, in which a diffusion barrier layer has to be applied to prohibit the diffusion of metals into the absorber, which adversely limits their ultimate flexibility and causes an additional step in the fabrication process. Third, lower processing temperatures also allow for more freedom on the design of device structure and the integration with other photovoltaic techniques, for example, multi-junction cells and inorganic–organic hybrid solar cells. The processing temperature of most of the organic materials is below 200 °C and therefore is not compatible with high annealing or selenization temperatures.

A 0.23% device was demonstrated by Steinhagen et al. utilizing the Au/CZTS/CdS/ZnO/ITO device structure without any annealing process. The structure and J–V curves are shown in Fig. 14a and b, respectively. Akhavan et al. found in the nanocrystal based solar cell work on CIGS counterpart that the Mo back contact used in the selenization process does not perform as well as Au. They suggested that the reason behind is the absence of MoSe2, which only forms at elevated temperatures, while Au has a higher work function to be a more suitable back contact to p-type absorbers. The Mo/CZTS contact will likely also suffer from the same issue, which possibly explains the choice of Au over Mo in the work of Steinhagen et al. High work function materials such as gold as back contacts exhibit better electrical contact with the P type CZTS material.

Inorganic–organic hybrid cells were demonstrated by Saha et al., reporting a 0.9% efficiency with a ITO/CZTS:PCBM/Ca/Al device structure. A CZTS:PCBM bulk heterojunction (BHJ) is employed here. The proposed band alignment of the hybrid device is shown in Fig. 14c. The J–V curve of the resulting device is shown in Fig. 14d. This result showed a comparable performance with the 3-D structure CIS nanocrystal/polymer and also CIS nanocrystal/small molecule solar cells. Based on the experience earned from the BHJ studies in OPV, the design of the CZTS nanocrystal and polymer properties, interface state of nanocrystal, LUMO and VBM energy band alignment, processing methods, the nanostructure of n-type layer and size of nanocrystals are key parameters for the further improvement of the hybrid solar cells.

In nanocrystal based solar cells of other material systems, progress has been made significantly in the recent years. Ning et al. has demonstrated the capability of PbS-based nanocrystals on photovoltaics with a power conversion efficiency of up to 7.4%. The breakthrough on nanocrystal surface passivation is one of the major improvements. With further studies and research, safe, environmental friendly, and earth abundant solar cells with decent power conversion efficiency and lower manufacturing cost can be realized in the future.

5 Summary and outlook

Nanocrystal dispersions represent a unique method for producing photovoltaic quality CZTSSe films. The assembly of
high quality kesterite crystallites in a carefully monitored environment prior to all aspects of film deposition allows for a nearly unprecedented level of control in designing and producing precursor materials and inks. Using nanoparticles that conform to a high quality kesterite structure has been instrumental in reducing the number of impurity phases and defects present in the final film as the crystallites grow and consume one another to produce the final material. However, the small particle sizes required for producing stable dispersions and smooth, continuous films invariably result in a need for post-deposition heat treatments in the presence of selenium or sulfur vapor to sinter the film and enlarge the grains to a scale that is acceptable for photovoltaic absorber materials. The ultimate success of this fabrication strategy relies on the synergistic optimization of both material synthesis and film treatments in ways that maximize the advantages of each. Perhaps the most difficult challenges remaining in the synthesis of nanoparticle inks are reliably controlling the rate at which the various metallic precursors incorporate into the growing particles, and productively managing the long chain ligands that stabilize the as-grown nanocrystal dispersions to avoid the presence of excessive carbon-based impurities in the completed film.

To date, solar cells based on CZTS nanoparticle inks have reached power conversion efficiencies of nearly 10% at the laboratory scale, putting them quite close to the record 11.1% efficiency for this material system. Further development will require a better understanding of the myriad of defect properties arising from the complex cation ordering arrangement, which currently produces a large detrimental open circuit voltage deficit and short minority carrier lifetime. Also, some other recently developed thin film materials, such as organic photovoltaics and hybrid perovskite solar cells, have begun producing rapidly increasing conversion efficiency values of up to 12% and 15%, respectively. The solution-phase processing and relative earth abundance of these material systems stand as stiff competition for the widespread adoption of CZTS solar cells and modules. The technique that ultimately offers the best mix of high performance, material abundance, easy fabrication, and long-term device stability will likely become the dominant thin film technology for next generation solar cell fabrication.

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