Towards highly efficient thin-film solar cells with a graded-bandgap CZTSSe layer

Ahmad, Faiz; Lakhtakia, Akhlesh; Anderson, Tom H; Monk, Peter B

Published in:
Journal of Physics: Energy

Link to article, DOI:
10.1088/2515-7655/ab6f4a

Publication date:
2020

Document Version
Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA):
Ahmad, F., Lakhtakia, A., Anderson, T. H., & Monk, P. B. (2020). Towards highly efficient thin-film solar cells with a graded-bandgap CZTSSe layer. Journal of Physics: Energy, 2(2), [025004]. https://doi.org/10.1088/2515-7655/ab6f4a

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
Towards highly efficient thin-film solar cells with a graded-bandgap CZTSSe layer

To cite this article: Faiz Ahmad et al 2020 J. Phys. Energy 2 025004

View the article online for updates and enhancements.
Towards highly efficient thin-film solar cells with a graded-bandgap CZTSSe layer

Faiz Ahmad, Akhlesh Lakhtakia, Tom H Anderson and Peter B Monk

1 NanoMM–Nanoengineered Metamaterials Group, Department of Engineering Science and Mechanics, Pennsylvania State University, University Park, PA 16802–6812, United States of America
2 Sektion for Konstruktion og Produktudvikling, Institut for Mekanisk Teknologi, Danmarks Tekniske Universitet, DK-2800 Kongens Lyngby, Denmark
3 Department of Mathematical Sciences, University of Delaware, Newark, DE 19716, United States of America
4 Author to whom any correspondence should be addressed.

E-mail: akhlesh@psu.edu

Keywords: bandgap grading, optoelectronic optimization, thin-film solar cell, CZTSSe solar cell, earth-abundant materials

Abstract

A coupled optoelectronic model was implemented along with the differential evolution algorithm to assess the efficacy of grading the bandgap of the Cu2ZnSn(Se1−ξTeξ)4 (CZTSSe) layer for enhancing the power conversion efficiency of thin-film CZTSSe solar cells. Both linearly and sinusoidally graded bandgaps were examined, with the molybdenum backreflector in the solar cell being either planar or periodically corrugated. Whereas an optimally graded bandgap can dramatically enhance the efficiency, the effect of periodically corrugating the backreflector is modest at best. An efficiency of 21.74% is predicted with sinusoidal grading of a 870 nm thick CZTSSe layer, in comparison to 12.6% efficiency achieved experimentally with a 2200 nm thick homogeneous CZTSSe layer. High electron-hole-pair generation rates in the narrow-bandgap regions and a high open-circuit voltage due to a wide bandgap close to the front and rear faces of the CZTSSe layer are responsible for the high enhancement of efficiency.

1. Introduction

As the worldwide demand for eco-responsible sources of cheap energy continues to increase for the betterment of an ever-increasing fraction of the human population [1], the cost of traditional crystalline-silicon solar cells continues to drop [2], as predicted earlier this decade [3]. While this is a laudable development, small-scale photovoltaic generation of energy must become ubiquitous for human progress to become truly unconstrained by energy economics. Thin-film solar cells are necessary for that to happen.

Currently, thin-film solar cells containing absorber layers made of either CIGS or CdTe are commercially dominant, even over their amorphous-silicon counterparts [4]. However, there is a strong concern about the planet-wide availability of indium (In) and tellurium (Te), both needed for CIGS and CdTe solar cells [5]. Furthermore, both In and cadmium (Cd) are toxic, leading to environmental concerns about their impact following disposal after use.

Thin-film solar cells must be made from materials that are abundant on our planet and that can extracted, processed, and discarded with low environmental cost. Cu2ZnSn(Se1−ξTeξ)4 (commonly referred as CZTSSe) is a p-type semiconductor than can be used in place of CIGS in a solar cell. CZTSSe comprises nontoxic and abundant materials [6]. But the record for the power conversion efficiency η of CZTSSe solar cells is only 12.6% [7, 8], which is substantially lower than the 22.6% record efficiency of CIGS solar cells [9, 10].

A low open-circuit voltage \( V_{oc} \) is the key limitation to high efficiency for CZTSSe solar cells [11–13]. This is due to

(i) more bandtail states in CZTSSe [14, 15];

(ii) the high electron-hole recombination rate inside the CZTSSe layer because of the short lifetime of minority carriers (electrons) [16];

© 2020 The Author(s). Published by IOP Publishing Ltd
The low lifetime of minority carriers shortens their diffusion length, thereby limiting the collection of minority carriers deep in the CZTSSe absorber layer [16, 18]. For example, the diffusion length of electrons is less than 1 𝜇m when the bandgap $E_g$ of CZTSSe is 1.15 eV (for $\xi \approx 0.41$), which means that a solar cell with a CZTSSe layer of thickness $L_s > 1 \mu m$ [18] will have a high series resistance [11, 19] that will have a deleterious effect on $\eta$. Reduction of $L_s$ is therefore desirable, all the more so because it will reduce material usage and enhance manufacturing throughput concomitantly. But, a smaller $L_s$ will reduce the absorption of incident photons. The common techniques for tackling this problem in thin-film solar cells are light trapping using nanostructures in front of the illuminated face of the solar cell [20–22], nanostructured backreflectors [23], and back-surface passivation [24]; however, let us note here that enhanced light trapping does not necessarily translate into higher efficiency [25, 26].

The issue of low $V_{oc}$, and therefore low $\eta$, of the CZTSSe solar cell can be tackled by grading the bandgap $E_g$ of the CZTSSe absorber layer in the thickness direction [27–34]. Since $E_g$ is a function of $\xi \in [0, 1]$, the parameter which quantifies the proportion of sulfur (S) relative to that of selenium (Se) in CZTSSe [6, 35, 36], the bandgap can be graded in the thickness direction by changing $\xi$ dynamically during fabrication [27]. Indeed, bandgap grading of the CZTSSe absorber layer has been experimentally demonstrated [27–29] to enhance both $V_{oc}$ and $\eta$ of CZTSSe solar cells, but we note that the maximum efficiency reported in [27–29] is 12.3%.

The experimental demonstration of increased efficiency due to bandgap grading is supported by theoretical studies. An empirical model recently suggested that a linearly graded 1150 nm thick absorber layer can deliver 16.9% efficiency. Several simulations performed with SCAPS software [37] have predicted efficiencies between 12.4% and 19.7% with absorber layers between 1000 and 3500 nm in thickness and the bandgap grading being linear [31], piecewise linear [32], parabolic [31, 34], or exponential [31, 33]. However, the SCAPS software is optically elementary in that it relies on the Beer–Lambert law [38] rather than on the correct solution of an optical boundary-value problem; a rigorous optoelectronic model is needed to examine bandgap grading for CZTSSe solar cells.

A coupled optoelectronic model has recently been devised for CIGS solar cells [26, 39]. This model was adapted for CZTSSe solar cells and used with the differential evolution algorithm (DEA) to maximize $\eta$ for linear and sinusoidal grading of the bandgap of the CZTSSe layer along the thickness direction (parallel to the z axis of a Cartesian coordinate system) in the thin-film solar cell depicted in figure 1. In the optical part of this model, the rigorous coupled-wave approach (RCWA) [40, 41] is used to determine the electron-hole-pair generation rate in the semiconductor region of the solar cell [26], assuming normal illumination by unpolarized polychromatic light endowed with the AM1.5G solar spectrum [42]. Then, in the electrical part of the model, the electron-hole-pair generation rate appears as a forcing function in the one-dimensional (1D) drift–diffusion equations [38, 43] applied to the semiconductor region. These equations are solved using a hybridizable discontinuous Galerkin (HDG) scheme [44–47] to determine the current density $I_{dev}$ and the electrical power density $P$ as functions of
the bias voltage \( V_{\text{ext}} \). In turn, the \( J_{\text{dev}}-V_{\text{ext}} \) and the \( P-V_{\text{ext}} \) curves yield the short-circuit current density \( J_{\text{sc}} \) along with \( V_{\text{oc}} \) and \( \eta \).

As shown in figure 1, we took the CZTSSe solar cell to comprise an antireflection coating of magnesium fluoride (MgF\(_2\)), followed by an aluminum-doped zinc oxide (AZO) layer as the front contact, a buffer layer of oxygen-deficient zinc oxide (od-ZnO), the ultrathin CdS layer, and the CZTSSe layer. The od-ZnO, CdS, and CZTSSe layers constitute the semiconductor region of the solar cell. Whereas the actual bandgap of CZTSSe was used for the optical part in our calculations, the bandgap was depressed in the electrical part in order to account for bandtail defects \(^{14, 15}\). The bandgap-dependent (i.e. \( \xi \)-dependent) defect density and electron affinity were used in the electrical calculations. The nonlinear Shockley–Read–Hall (SRH) and radiative processes for electron-hole recombination were also incorporated \(^{38, 43}\). The Mo backreflector was assumed to be periodically corrugated along a fixed axis (designated as the \( x \) axis) normal to the \( z \) axis. A thin layer of aluminum oxide (Al\(_2\)O\(_3\)) was inserted between the CZTSSe layer and the Mo backreflector, as has been experimentally shown to prevent the formation of a Mo layer that enhances the back-contact electron-hole recombination rate and depresses \( \eta \) \(^{48}\). The efficiency \( \eta \) was maximized for (a) homogeneous, (b) linearly graded, as well as (c) sinusoidally graded CZTSSe layers using the differential evolution algorithm (DEA) \(^{49}\). The role of traps at the CdS/CZTSSe interface was assessed by incorporating a surface-defect layer \(^{50}\) with higher defect density.

This paper is organized as follows. The optical description of the solar cell of figure 1 is presented in section 2.1 along with the approach taken for optical calculations. The electrical description of the solar cell is discussed in section 2.2. Optimization for maximum efficiency is briefly discussed in section 2.3. Section 3.1 compares the efficiency of the conventional solar cell with a 2200 nm thick homogeneous CZTSSe layer \(^{7}\) with that predicted by the coupled optoelectronic model. The effects of the Al\(_2\)O\(_3\) layer and the CdS/CZTSSe interface recombination rate on the solar-cell performance are discussed in sections 3.2 and 3.3, respectively. Section 3.4 provides the optimal configurations of solar cells with a homogeneous CZTSSe layer and a planar backreflector, section 3.5 for solar cells with a homogeneous CZTSSe layer and a periodically corrugated backreflector, and section 3.6 for solar cells with a linearly graded CZTSSe layer and either a planar or a periodically corrugated backreflector, while optimal configurations of solar cells with a sinusoidally graded CZTSSe layer and either a planar or a periodically corrugated backreflector are presented in section 3.7. Concluding remarks are provided in section 4.

2. Optoelectronic modeling and optimization

2.1. Optical theory in brief

The CZTSSe solar cell occupies the region \( \Lambda \): \([x, y, z]|-\infty < x < \infty, -\infty < y < \infty, 0 < z < L_1\)\), the half spaces \( z < 0 \) and \( z > L_1 \) being occupied by air. The reference unit cell of this structure, shown in figure 1, occupies the region \( \mathcal{R} \): \([x, y, z]|-L_x/2 < x < L_x/2, -\infty < y < \infty, 0 < z < L_1\). The region \( 0 < z < L_w = 210 \text{ nm} \) consists of a 110 nm thick antireflection coating \(^{51}\) made of MgF\(_2\) layer \(^{52}\) and a 100 nm thick AZO layer \(^{53}\) as the front contact. The region \( L_w < z < L_w + L_{\text{ZnO}} \) is a 100 nm thick buffer layer of oxygen-deficient zinc oxide (od-ZnO) \(^{54}\). Oxygen deficiency during the deposition of ZnO makes it an \( n \)-type semiconductor \(^{55}\). The region \( L_w + L_{\text{ZnO}} < z < L_w + L_{\text{ZnO}} + L_{\text{CdS}} \) is a 50 nm thick layer of \( n \)-type CdS \(^{56}\) that forms a junction with the \( p \)-type CZTSSe layer of thickness \( L_e \in [100, 2200] \text{ nm} \) and a bandgap \( E_g(z) \) that can vary with \( z \). The region \( L_d + L_a + L_g < z < L_1 \) is occupied by Mo \(^{57}\) of permittivity \( \varepsilon_m(\lambda_0) \), where \( \lambda_0 \) is the free-space wavelength. The thickness \( L_m = L_1 - (L_d + L_a + L_g) = 500 \text{ nm} \) was chosen to be significantly larger than the electromagnetic penetration depth \(^{58}\) of Mo across the visible spectrum. A thin Al\(_2\)O\(_3\) \(^{59}\) layer of thickness \( L_d = 20 \text{ nm} \) and permittivity \( \varepsilon_d(\lambda_0) \) exists between the Mo backreflector and the CZTSSe absorber layer \(^{48}\).

The region \( L_d + L_a < z < L_d + L_a + L_g \) has a rectangular metallic grating with period \( L_a \) along the \( x \) axis. In this region, the permittivity is given by

\[
\varepsilon_g(x, z, \lambda_0) = \begin{cases} 
    \varepsilon_m(\lambda_0), & |x| < \zeta L_x/2, \\
    \varepsilon_d(\lambda_0), & |x| \geq \zeta L_x/2,
\end{cases}
\]

\( z \in (L_d + L_a, L_d + L_a + L_g) \),

(1)

with \( \zeta \in (0, 1) \) as the duty cycle. The grating is absent for \( \zeta \in \{0, 1\} \).

The linearly nonhomogeneous bandgap can be either backward graded or forward-graded. For backward grading,
where $A$ is an amplitude, $E_{g,\text{min}}$ is the minimum bandgap, and $E_{g,\text{max}}$ is the maximum bandgap; $A = 0$ represents a homogeneous CZTSSe layer. For forward grading,

$$E_d(z) = E_{g,\text{min}} + A(E_{g,\text{max}} - E_{g,\text{min}}) \frac{z - (L_w + L_{\text{ZnO}} + L_{\text{CdS}})}{L},$$

where $z \in [L_w + L_{\text{ZnO}} + L_{\text{CdS}}, L_d]$, (2)

Two representative bandgap profiles are shown in figures 2(a), (b).

For the sinusoidally graded bandgap,

$$E_d(z) = E_{g,\text{min}} + A(1.49 - E_{g,\text{min}}) \times \left\{ \frac{1}{2} \left[ \sin \left( 2\pi K \frac{z - (L_w + L_{\text{ZnO}} + L_{\text{CdS}})}{L} - 2\pi \psi \right) + 1 \right] \right\}^\alpha ,$$

where the integer $K$ is the number of periods in the CZTSSe layer, $\psi \in [0, 1]$ describes a relative phase shift, and $\alpha > 0$ is a shaping parameter. Two representative profiles are provided in figures 2(c), (d). As thin-film solar cells are fabricated using vapor-deposition techniques [60], graded bandgap profiles could be physically realized by adjusting the sulfur-to-selenium ratio in the precursor and thus varying the composition parameter $\xi \in [0, 1]$ during the deposition process [27, 28, 61]. Optical spectra of the relative permittivities of all materials used in the solar cell are provided in the appendix.

The RCWA [40, 41] was used for monochromatic calculations. The electric field phasor $E(x, z, \lambda_0)$ and the magnetic field phasor $H(x, z, \lambda_0)$, created everywhere inside the solar cell due to illumination by an unpolarized plane wave normally incident on the plane $z = 0$, were calculated with $E_0 = 4\sqrt{15}\pi \text{ V m}^{-1}$ being the amplitude of the incident electric field. The region $R$ was partitioned into a sufficiently large number of slices along the $z$ axis, in order to implement the RCWA. Although each slice was homogeneous along the $z$ axis, it could be periodically nonhomogeneous along the $x$ axis. The slice thickness was chosen by trial and error such that the useful solar absorptance [62] converged with a preset tolerance of $\pm 1\%$. The usual boundary conditions on the continuity of the tangential components of the electric and magnetic field phasors were enforced on the
plane \( z = 0 \) to match the internal field phasors to the sum of the incident and reflected field phasors. The same was done to match the internal field phasors to the transmitted field phasors on the plane \( z = L_t \). Detailed descriptions of the RCWA for solar cells are available [41, 62, 63].

Suppose that every photon absorbed in the semiconductor region \( L_w < z < L_d \) excites an electron-hole pair. Then, the \( x \)-averaged electron-hole-pair generation rate is [26]

\[
G(x) = \sqrt{\frac{\hbar \varepsilon_0}{\varepsilon_0}} \int_{-L_d/2}^{L_d/2} \left[ \int_{\lambda_{0,min}}^{\lambda_{0,max}} \text{Im} \{ \varepsilon(x, z, \lambda_0) \} [E(x, z, \lambda_0)]^2 S(\lambda_0) \, d\lambda_0 \right] dx
\]

for \( z \in [L_w, L_d] \), where \( \hbar \) is the reduced Planck constant, \( \varepsilon_0 \) is the free-space permittivity, \( \mu_0 \) is the free-space permeability, \( S(\lambda_0) \) is the AM1.5G solar spectrum [42], \( \lambda_{0,min} = 300 \) nm, and \( \lambda_{0,max} = (1240 / E_{g,min}) \) nm with \( E_{g,min} \) stated in eV. Averaging about the \( x \) axis can be justified for two reasons. First, any current generated parallel to the \( x \) axis shall be negligibly small because the solar cell operates under the influence of a \( z \)-directed electrostatic field due to the application of \( V_m \). Second, for electrostatic analysis \( L_s \sim 500 \) nm is very small in comparison to the lateral dimensions of the solar cell.

### 2.2. Electrical theory in brief

For electrical modeling, only the region \( L_w < z < L_d \) has to be considered, because electron-hole pair generation occurs in the CZTSSe, od-ZnO, and CdS layers only. With a bandgap of \( 3.3 \) eV, od-ZnO absorbs solar photons with energies corresponding to \( \lambda_0 \in [300, 376] \) nm. Likewise, CdS absorbs solar photons with energies corresponding to \( \lambda_0 \in [300, 517] \) nm, as its bandgap is \( 2.4 \) eV. The planes \( z = L_w \) and \( z = L_d \) were assumed to be ideal ohmic contacts, as we are not interested in how the solar cell interacts with an external circuit.

The electron quasi-Fermi level

\[
E_{f_e}(z) = E_c(z) + (k_B T / q_e) \ln \left[ n(z) / N_c(z) \right]
\]

and the hole quasi-Fermi level

\[
E_{f_h}(z) = E_v(z) - (k_B T / q_h) \ln \left[ p(z) / N_v(z) \right]
\]

depend on \( N_c(z) \) as the density of states in the conduction band, \( N_v(z) \) as the density of states in the valence band, \( E_c(z) = E_0 - [\phi(z) + \chi(z)] \) as the conduction band-edge energy, \( E_v(z) = E_g(z) - E_{fg}(z) \) as the valence band-edge energy, \( \phi(z) \) as the dc electric potential, \( \chi(z) \) as the bandgap-dependent electron affinity, \( k_B \) as the Boltzmann constant, and \( T \) as the absolute temperature. The reference energy level \( E_0 \) is arbitrary.

The gradients of the quasi-Fermi levels drive the electron–current density \( J_e(z) \) and the hole-current density \( J_h(z) \); thus,

\[
\begin{align*}
J_e(z) &= q_e \mu_e n(z) \frac{dE_{f_e}(z)}{dz}, \\
J_h(z) &= q_h \mu_h p(z) \frac{dE_{f_h}(z)}{dz},
\end{align*}
\]

\( z \in (L_w, L_d) \),

\( \mu_e \) is the electron mobility, and \( \mu_h \) is the hole mobility. According to the Boltzmann approximation [43],

\[
\begin{align*}
n(z) &= n_i(z) \exp \left[ q_e [E_c(z) - E_f(z)] / k_B T \right], \\
p(z) &= n_i(z) \exp \left[ -q_h [E_v(z) - E_f(z)] / k_B T \right],
\end{align*}
\]

where

\[
n_i(z) = \sqrt{N_c(z) N_v(z)} \exp \left[ q_e E_f(z) / 2k_B T \right]
\]

is the intrinsic charge-carrier density and

\[
E_f(z) = (1/2) \left[ E_c(z) + E_v(z) - (k_B T / q_e) \ln \left[ N_c(z) / N_v(z) \right] \right]
\]

is the intrinsic energy. Both \( N_c(z) \) and \( N_v(z) \) are functions of \( z \) because they depend on the bandgap but we took them to be independent of \( z \), following Hironiwa et al [32], because bandgap-dependent values are unavailable for CZTSSe.
The 1D drift-diffusion model comprises the three differential equations [43], section 4.6

\[
\begin{align*}
\frac{d}{dz} n(z) &= -q_e [G(z) - R(n, p; z)] \\
\frac{d}{dz} p(z) &= q_e [G(z) - R(n, p; z)] \\
\varepsilon_0 &\left[ \frac{d}{dz} \varepsilon_{dc}(z) \frac{d}{dz} \phi(z) \right] = -q_e [N_r(z) + N_0(z) + p(z) - n(z)]
\end{align*}
\]

(12)

under steady-state conditions, with \( R(n, p; z) \) as the electron-hole-pair recombination rate, \( N_r(z) \) as the defect density or the trap density, \( N_0(z) \) as the doping density which is positive for donors and negative for acceptors, and \( \varepsilon_{dc}(z) \) as the dc relative permittivity. Both \( N_r \) and \( \varepsilon_{dc} \) depend on \( \xi \) and, therefore, on \( E_s \). All three differential equations have to be solved simultaneously for \( z \in (L_w, L_d) \).

The radiative recombination rate is given by

\[ R_{\text{rad}}(n, p; z) = R_b[n(z)p(z) - n_i^2(z)], \]

(13)

where \( R_b \) is the radiative recombination coefficient [38, 43]. The SRH recombination rate is given by

\[ R_{\text{SRH}}(n, p; z) = \frac{n(z)p(z) - n_i^2(z)}{\tau_p(z)[n(z) + n_i(z)] + \tau_n(z)[p(z) + p_i(z)]}, \]

(14)

where \( n_i(z) \) is the electron density and \( p_i(z) \) is the hole density at the trap energy level \( E_T \); the electron lifetime \( \tau_p(z) = 1/[\tau_i n_0(z) N_r(z)] \) depends on the electron-capture cross section \( \tau_i \); the hole lifetime \( \tau_n(z) = 1/[\tau_i n_0(z) N_r(z)] \) depends on the hole-capture cross section \( \tau_i \); and \( V_{th} \) is the mean thermal speed of all charge carriers [38, 43]. The total recombination rate then is \( R(n, p; z) = R_{\text{rad}}(n, p; z) + R_{\text{SRH}}(n, p; z) \).

Dirichlet boundary conditions on \( n(z), p(z) \), and \( \phi(z) \) at the planes \( z = L_w \) and \( z = L_d \) were taken to be charge-free and in local quasi-thermal equilibrium [38]. The bias voltage \( V_{ext} \) was taken to be applied at the plane \( z = L_d \).

The HDG scheme [45, 46, 64] was used to solve all three differential equations. This scheme works well for solar cells containing heterojunction interfaces [47]. All \( z \)-dependent variables are discretized in this scheme using discontinuous finite elements in a space of piecewise polynomials of a fixed degree. We used the Newton–Raphson method to solve the resulting system for \( n(z), p(z) \), and \( \phi(z) \) [65].

Table 1 provides the values of electrical parameters used for od-ZnO, CdS, and CZTSSe for \( \xi \in [0, 1] \).

| Symbol (unit) | od-ZnO [66] | CdS [66] | CZTSSe [6, 12] |
|--------------|-------------|----------|----------------|
| \( E_s \) (eV) | 3.3 | 2.4 | 0.91 + 0.58\( \xi \) (optical part) \\
| \( \chi \) (eV) | 4.4 | 4.2 | 0.91 + 0.44\( \xi \) (electrical part)* |
| \( N_r \) (cm\(^{-3}\)) | \( 1 \times 10^{17} \) (donor) | \( 5 \times 10^{17} \) (donor) | \( 1 \times 10^{16} \) (acceptor) |
| \( N_0 \) (cm\(^{-3}\)) | 3 \times 10^{18} | 1.3 \times 10^{18} | 7.8 \times 10^{17} |
| \( N_s \) (cm\(^{-3}\)) | 1.7 \times 10^{18} | 9.1 \times 10^{18} | 4.5 \times 10^{18} |
| \( \mu_n \) (cm\(^2\)V\(^{-1}\)s\(^{-1}\)) | 100 | 72 | 40 |
| \( \mu_p \) (cm\(^2\)V\(^{-1}\)s\(^{-1}\)) | 31 | 20 | 12.6 |
| \( \varepsilon_{dc} \) | 9 | 5.4 | 14.9 - 1.2\( \xi \) |
| \( N_r \) (cm\(^{-3}\)) | \( 10^{16} \) | \( 10^{12} \) | \( (1.35 + 98.65\xi) \times 10^{15} \) |
| \( E_s \) (midgap) | midgap | midgap | midgap |
| \( \sigma_r \) (cm\(^2\)) | \( 5 \times 10^{-13} \) | \( 5 \times 10^{-13} \) | \( 10^{-11} \) |
| \( \sigma_f \) (cm\(^2\)) | \( 10^{-14} \) | \( 10^{-15} \) | \( 10^{-14} \) |
| \( R_b \) (cm\(^{-3}\)s\(^{-1}\)) | \( 10^{-10} \) | \( 10^{-10} \) | \( 10^{-10} \) |
| \( v_i \) (cm s\(^{-1}\)) | \( 10^7 \) | \( 10^7 \) | \( 10^7 \) |

**Note.** *E_s* is artificially reduced in the electrical part so as to account for bandtail states.

The effect of bandtail states, which effectively narrow the bandgap, was incorporated [14, 15] by reducing the bandgap of CZTSSe for electrical calculations. Whereas \( E_s = 0.91 + 0.58\xi \in [0.91, 1.49] \) eV was used for CZTSSe in the optical part of the coupled optoelectronic model, \( E_s = 0.91 + 0.44\xi \in [0.91, 1.35] \) eV was used in the electrical part [14, 15].
2.3. Optoelectronic optimization
The total current density \( J_{\text{sc}}(x) + J_{\text{f}}(x) \) equals \( J_{\text{dev}} \) everywhere in the od-ZnO, CdS, and CZTSSe layers, under steady-state conditions. When the solar cell is connected to an external circuit, \( J_{\text{dev}} \) is the current density delivered by the former to the latter. The short-circuit current density \( J_{\text{sc}} \) is the value of \( J_{\text{dev}} \) when \( V_{\text{ext}} = 0 \) and the open-circuit voltage \( V_{\text{oc}} \) is the value of \( V_{\text{ext}} \) such that \( J_{\text{dev}} = 0 \). The power density is defined as \( P = J_{\text{dev}} V_{\text{ext}} \); the maximum power density \( P_{\text{max}} \) obtainable from the solar cell is the highest value of \( P \) on the \( P - V_{\text{ext}} \) curve; and \( \eta = P_{\text{max}} / P_{\text{in}} \), where \( P_{\text{in}} = 1000 \text{ W m}^{-2} \) is the integral of \( S(\lambda_0) \) over the solar spectrum. The fill factor \( FF = P_{\text{max}} / (V_{\text{oc}} J_{\text{sc}}) \) is commonly encountered in the solar-cell literature.

The DEA [49] was used to optimize \( \eta \) with respect to certain geometric and bandgap parameters, using a custom algorithm implemented with MATLAB® version R2017b.

3. Numerical results and discussion

3.1. Conventional CZTSSe solar cell (model validation)
Our coupled optoelectronic model was validated by comparison with experimental results available for the conventional MgF\(_2\)/AZO/od-ZnO/CdS/CZTSSe/Mo(S\(_2\)Se\(_1\),\( \_\))\(_2\)/Mo solar cell containing a 2000 nm thick homogeneous CZTSSe layer and a planar backreflector [7]. In this solar cell, a 200 nm thick Mo(S\(_2\)Se\(_1\),\( \_\))\(_2\) layer with defect density \( N_{\text{f}} = 10^{18} \text{ cm}^{-3} \) is present whereas the Al\(_2\)O\(_3\) layer is absent in relation to figure 1, and we made appropriate modifications for the validation. All other relevant electrical parameters of Mo(S\(_2\)Se\(_1\),\( \_\))\(_2\) were taken to be the same as that of CZTSSe, except that \( E_\text{g} = 1.57 + 0.31 \xi \text{ eV} \) [67] was used for Mo(S\(_2\)Se\(_1\),\( \_\))\(_2\) in both the optical and electric parts of the coupled optoelectronic model. The relative permittivity of Mo(S\(_2\)Se\(_1\),\( \_\))\(_2\) in the optical regime is provided in appendix.

The values of \( J_{\text{sc}}, V_{\text{oc}}, FF, \) and \( \eta \) obtained from our coupled optoelectronic model for \( \xi \in \{0, 0.38, 1\} \) are provided in table 2 along with the corresponding experimental data [7, 15, 19]. According to this table, the model’s predictions are in reasonable agreement with the experimental data, the variances being very likely due to differences between the optical and electrical properties inputted to the model from those realized in practice. As interface defects are not explicitly considered in our model, all the experimentally observed features can be adequately accounted for by the bulk properties of CZTSSe, which is also in accord with the empirical model provided by Gokmen et al [68].

In order to further elaborate the role of the Mo(S\(_2\)Se\(_1\),\( \_\))\(_2\) layer, we lowered its thickness from 200 to 100 nm but increased the thickness \( L_{\text{a}} \) of the CZTSSe absorber layer from 2000 to 2100 nm. The composition parameter \( \xi \) was taken to be 0.38 for the Mo(S\(_2\)Se\(_1\),\( \_\))\(_2\) layer as well as for the CZTSSe layer, but other parameters remained the same as for the model’s results stated in table 2. The model-predicted efficiency increased from 11.15% to 11.23%, indicating the minor role of the thickness of the Mo(S\(_2\)Se\(_1\),\( \_\))\(_2\) layer.

3.2. Effect of Al\(_2\)O\(_3\) layer
The incorporation of an ultrathin Al\(_2\)O\(_3\) layer below the CZTSSe layer prevents the formation of a Mo(S\(_2\)Se\(_1\),\( \_\))\(_2\) layer and thereby enhances performance [48]. Removing the Mo(S\(_2\)Se\(_1\),\( \_\))\(_2\) layer and reverting to the solar cell

| \( \xi \) | \( J_{\text{sc}} \) (mA cm\(^{-2}\)) | \( V_{\text{oc}} \) (mV) | FF (%) | \( \eta \) (%) |
|---|---|---|---|---|
| 0 | Model | 38.31 | 361 | 65 | 8.96 |
|  | Experiment | 36.4 | 412 | 62 | 9.33 |
| 0.38 | Model | 32.42 | 509 | 69 | 11.15 |
|  | Experiment | 35.2 | 513.4 | 69.8 | 12.6 |
| 1 | Model | 17.86 | 606 | 60.7 | 6.61 |
|  | Experiment | 16.9 | 637 | 61.7 | 6.7 |
depicted in figure 1, we optimized the CZTSSe solar cell with and without a 20 nm thick Al₂O₃ layer between the CZTSSe layer and a planar Mo backreflector. Values of $I_{sc}$, $V_{oc}$, $FF$, and $\eta$ obtained from our coupled optoelectronic model for $L_s = 2200$ nm are presented in table 3. The optimal efficiency is 11.76% with the Al₂O₃ layer and 11.37% without it. Thus, the Al₂O₃ layer enhances $\eta$ slightly, and concurrent improvements in both $I_{sc}$ and $V_{oc}$ can also be noted in table 3. Hence, the 20 nm thick Al₂O₃ layer was incorporated in the solar cell for all of the following results.

### 3.3. Effect of surface recombination on Cds/CZTSSe interface

A 10-nm-thin surface-defect layer was inserted between the Cds and CZTSSe layers to investigate the effect of surface recombination at that interface on the performance of the solar cell depicted in figure 1. The CZTSSe layer was taken to be homogeneous with thickness $L_s \in [100, 2200]$ nm and all other parameters as reported in table 1. The surface-defect density was fixed at $10^{12}$ cm$^{-2}$ but the mean thermal speed was varied between $10^2$ cm s$^{-1}$ and $10^7$ cm s$^{-1}$ in the surface-defect layer, with all other characteristics of this layer taken to be the same as of the CZTSSe layer.

The optimal value of $\xi = 0.51$ for $L_s = 100$ nm. On inserting the surface-defect layer, the efficiency reduced from 7.41% to: (i) 7.31% when $v_{th} = 10^2$ cm s$^{-1}$ in the surface-defect layer and (ii) 7.22% when $v_{th}$ is $10^7$ cm s$^{-1}$ in the surface-defect layer. The optimal value of $\xi = 0.50$ for $L_s = 2200$ nm. On inserting the surface-defect layer, the efficiency reduced from 11.15% to: (i) 11.07% when $v_{th} = 10^2$ cm s$^{-1}$ in the surface-defect layer and (ii) 11.02% when $v_{th}$ is $10^7$ cm s$^{-1}$ in the surface-defect layer. Similar efficiency reductions were predicted for intermediate values of $L_s$. These efficiency reductions are so small that the surface-defect layer can be ignored with minimal consequences. Therefore, we neglected surface recombination on the Cds/CZTSSe interface for all results presented from now onwards.

### 3.4. Optimal solar cell: homogeneous bandgap and planar backreflector

Next, we optimized a solar cell in which the CZTSSe layer is homogeneous ($A = 0$) and the backreflector is planar ($L_g = 0$), in order to highlight the advantage of the nonhomogeneous CZTSSe layer.

For a fixed value of $L_s$, the parameter space for optimizing $\eta$: $E_{g,\text{min}} \in [0.91, 1.49]$ eV (for the optical part$^5$). With $L_s = 2200$ nm, the maximum efficiency predicted for $A = 0$ and $L_g = 0$ is 11.76% when $E_{g,\text{min}} = 1.20$ eV. The corresponding values of $I_{sc}$, $V_{oc}$, and $FF$ are 30.00 mA cm$^{-2}$, 557 mV, and 70.3%, respectively. Incidentally, the efficiency becomes lower for $E_{g,\text{min}} > 1.2$ eV because of

(a) the narrowing of the portion of the solar spectrum available for photon absorption [69] due to the blue shift of $\lambda_{g,\text{max}}$, and
(b) the increased recombination due to increase in $N_f$ caused by the higher value of $\xi$ [6, 12, 19].

Next, we considered $L_s \in [100, 2200]$ nm also as a parameter for maximizing $\eta$. The highest efficiency predicted is 11.84%, produced by a solar cell with a 1200 nm thick CZTSSe layer with an optimal bandgap of $E_{g,\text{min}} = 1.21$ eV. The values of $I_{sc}$, $V_{oc}$, and $FF$ corresponding to this optimal design are 30.13 mA cm$^{-2}$, 558 mV, and 70.3%, respectively.

In order to compare the performance of the solar cell with optimal $L_s$, values of $E_{g,\text{min}}$ (for the optical part), $J_{sc}$, $V_{oc}$, $FF$, and $\eta$ predicted by the coupled optoelectronic model are presented in table 4 for seven representative values of $L_s$. The maximum efficiency increases to 11.84% as $L_s$ increases to 1200 nm, but decreases at a very slow rate with further increase of $L_s$. The efficiency increase with $L_s$ for $L_s < 1200$ nm is due to the increase in volume available to absorb photons. The efficiency reduction for $L_s > 1200$ nm is due to reduced charge-carrier collection arising from short diffusion length of minority charge carriers in CZTSSe being smaller than $L_s$ [18].

---

$^5$ Throughout section 3, the values of $E_g$ stated for the CZTSSe layer pertain to the optical part of the coupled optoelectronic model. Knowing $E_g$ for the optical part, one can use table 1 to find $\xi$ and, therefore, $E_g$ for the electrical part of the coupled optoelectronic model.
Notably, the optimal bandgap of the CZTSSe layer fluctuates in a small range (i.e. [1.18, 1.21] eV), despite a 22-fold increase of $L_x$.

### 3.5. Optimal solar cell: homogeneous bandgap and periodically corrugated backreflector

Next, we carried out the optoelectronic optimization of solar cells with a homogeneous CZTSSe layer ($A = 0$), as in section 3.4, but with a periodically corrugated backreflector. The parameter space for optimizing $\eta$ was set up as: $L_x \in [100, 2200]$ nm, $E_{g,\text{min}} \in [0.91, 1.49]$ eV for the optical part, $L_g \in [1, 550]$ nm, $\zeta \in (0, 1)$, and $L_x \in [100, 1000]$ nm.

The values of $\bar{J}_sc$, $V_{oc}$, $FF$, and $\eta$ predicted by the coupled optoelectronic model are presented in Table 5 for seven representative values of $L_x$. The values of $E_{g,\text{min}}$, $L_g$, $\zeta$, and $L_x$ for the optimal designs are also provided in the same table.

On comparing Tables 4 and 5, we found that periodic corrugation of the Mo backreflector slightly improves $\eta$ for $L_x \in [100, 600]$ nm. For example, relative to the planar backreflector, the efficiency increases from 10.38% to 10.72% when $L_x = 300$ nm, the other parameters being $L_g = 100$ nm, $\zeta = 0.5$, $L_x = 500$ nm, and $E_{g,\text{min}} = 1.20$ eV. No improvement in efficiency was found for $L_x > 600$ nm by the use of a periodically corrugated backreflector. The optimal bandgap of CZTSSe remains the same as with the planar backreflector in section 3.4; also, the optimal corrugation parameters lie in narrow ranges: $L_g \in [99, 105]$ nm, $\zeta \in [0.5, 51]$, and $L_x \in [500, 510]$ nm.

### 3.6. Optimal solar cell: linearly graded bandgap and planar/periodically corrugated backreflector

Next, we considered the maximization of $\eta$ when the bandgap of the CZTSSe layer is linearly graded, according to either equation (2) or (3), and the backreflector is either planar or periodically corrugated.

#### 3.6.1. Backward grading

Equation (2) is used for backward grading, i.e. the bandgap near the front contact is larger than the bandgap near the back contact for $A > 0$. Optoelectronic optimization yielded $A = 0$, i.e. a homogeneous bandgap, whether the backreflector is planar or periodically corrugated. Therefore, the optimized results provided in sections 3.4 and 3.5 also apply for backward bandgap grading of the CZTSSe layer.
Table 6. Predicted parameters of the optimal CZTSSe solar cell with a specified value of $L_s \in [100, 2200]$ nm, when the CZTSSe layer is linearly graded ($A \neq 0$) according to equation (3) and the Mo backreflector is periodically corrugated. The values of $E_{g,\text{min}}$ and $E_{g,\text{max}}$ provided pertain to the optical part of the model.

| $L_s$ (nm) | $E_{g,\text{min}}$ (eV) | $E_{g,\text{max}}$ (eV) | $A$ | $I_g$ (nm) | $I_{oc}$ (nm) | $I_{sc}$ (mA cm$^{-2}$) | $V_{oc}$ (mV) | $FF$ (%) | $\eta$ (%) |
|-----------|-----------------|-----------------|-----|----------|----------|-----------------|--------|-------|-------|
| 100       | 0.92            | 1.49            | 0.99 | 100      | 0.50     | 510             | 20.24  | 544   | 76.0  | 8.44  |
| 200       | 0.92            | 1.49            | 1.00 | 100      | 0.50     | 500             | 27.42  | 572   | 74.5  | 11.69 |
| 300       | 0.91            | 1.49            | 0.99 | 100      | 0.50     | 510             | 29.88  | 592   | 74.0  | 13.01 |
| 400       | 0.92            | 1.49            | 0.99 | 100      | 0.51     | 550             | 31.39  | 603   | 73.0  | 13.91 |
| 600       | 0.91            | 1.49            | 1.00 | 100      | 0.50     | 502             | 32.98  | 612   | 73.6  | 14.87 |
| 1200      | 0.93            | 1.49            | 0.99 | 100      | 0.51     | 500             | 35.02  | 617   | 73.5  | 15.90 |
| 2200      | 0.91            | 1.49            | 0.99 | 100      | 0.51     | 500             | 36.72  | 628   | 74.0  | 17.07 |

Table 7. Predicted parameters of the optimal CZTSSe solar cell with a specified value of $L_s \in [100, 2200]$ nm, when the CZTSSe layer is linearly graded ($A \neq 0$) according to equation (3) and the Mo backreflector is planar ($L_g = 0$). The values of $E_{g,\text{min}}$ and $E_{g,\text{max}}$ provided pertain to the optical part of the model.

| $L_s$ (nm) | $E_{g,\text{min}}$ (eV) | $E_{g,\text{max}}$ (eV) | $A$ | $I_{oc}$ (mA cm$^{-2}$) | $V_{oc}$ (mV) | FF (%) | $\eta$ (%) |
|-----------|-----------------|-----------------|-----|-----------------|--------|-------|-------|
| 100       | 0.91            | 1.49            | 0.99 | 19.34           | 550    | 76.8  | 8.18  |
| 200       | 0.92            | 1.49            | 0.99 | 26.18           | 568    | 74.2  | 11.04 |
| 300       | 0.91            | 1.49            | 0.99 | 30.07           | 590    | 73.2  | 13.00 |
| 400       | 0.91            | 1.49            | 0.99 | 31.16           | 601    | 73.4  | 13.75 |
| 600       | 0.92            | 1.49            | 0.99 | 33.17           | 610    | 73.6  | 14.92 |
| 1200      | 0.93            | 1.49            | 0.99 | 35.02           | 617    | 73.5  | 15.90 |
| 2200      | 0.91            | 1.49            | 0.99 | 36.72           | 628    | 74.0  | 17.07 |

3.6.2. Forward grading

On the other hand, when equation (3) is used, the bandgap near the front contact is smaller than the bandgap near the back contact for $A > 0$. The parameter space used for optimizing $\eta$ is: $L_s \in [100, 2200]$ nm, $E_{g,\text{min}} \in [0.91, 1.49]$ eV, $E_{g,\text{max}} \in [0.91, 1.49]$ eV, $A \in [0, 1]$, $L_g \in [1, 550]$ nm, $\zeta \in (0, 1)$, and $L_A \in [100, 1000]$ nm with the condition that $E_{g,\text{max}} \geq E_{g,\text{min}}$. The values of $J_{oc}$, $V_{oc}$, $FF$, and $\eta$ predicted by the coupled optoelectronic model are presented in table 6 for seven representative values of $L_s$. The values of $E_{g,\text{min}}$, $E_{g,\text{max}}$, $A$, $I_g$, $\zeta$ and $L_s$ for the optimal designs are also provided in the same table. The corresponding data for optimal solar cells with a planar backreflector ($L_g = 0$) are provided for comparison in table 7.

Just as in section 3.5, on comparing tables 6 and 7, we found that periodic corrugation of the Mo backreflector slightly improves $\eta$ for $L_s \lesssim 600$ nm. Thus, for $L_s = 200$ nm, the maximum efficiency predicted is 11.04% with a planar backreflector and 11.69% with a periodically corrugated backreflector. Whether the backreflector is planar or periodically corrugated, the optimal parameters for forward grading are: $E_{g,\text{min}} = 0.92$ eV, $E_{g,\text{max}} = 1.49$ eV, and $A \approx 1$. The optimal parameters for the periodically corrugated backreflector for $L_s = 200$ nm are: $L_g = 100$ nm, $\zeta = 0.50$, and $L_A = 500$ nm. No improvement in efficiency was found for $L_s > 600$ nm by the use of a periodically corrugated backreflector.

The highest efficiency predicted in tables 6 and 7 is 17.07%, which arises when $L_s = 2200$ nm, $E_{g,\text{min}} = 0.91$ eV, $E_{g,\text{max}} = 1.49$ eV, and $A = 0.99$ for both planar ($L_g = 0$) and periodically corrugated backreflectors. The values of $J_{oc}$, $V_{oc}$, and $FF$ corresponding to this optimal design are 36.72 mA cm$^{-2}$, 628 mV, and 74.0%, respectively. Relative to the optimal homogeneous CZTSSe layer (section 3.4), the maximum efficiency increases from 11.84% to 17.07% (a relative increase of 44.1%) with forward grading of the CZTSSe layer; concurrently, $J_{oc}$, $V_{oc}$, as well as $FF$ are also enhanced.

The optimal values of $E_{g,\text{min}} \in [0.91, 0.93]$ eV and $A \in [0.99, 1.0]$ in tables 6 and 7, and the optimal values of $E_{g,\text{max}}$ are independent of $L_s$, whether the backreflector is planar or periodically corrugated. Also, the optimal corrugation parameters are very weakly dependent on $L_s$: $L_g = 100$ nm, $\zeta \in [0.5, 51]$, and $L_A \in [500, 550]$ nm.

No difference could be discerned in the semiconductor regions of the forward-graded solar cells with the highest efficiency in tables 6 and 7, the CZTSSe absorber layer being 2200 nm thick whether the backreflector is planar or periodically corrugated. Spatial profiles of $E_g(z)$ and $\chi(z)$ are provided in figures 3(a), (b), whereas figure 3(c) presents the spatial profiles of $E_s(z)$, $E_g(z)$, and $E_i(z)$. The spatial variations of $E_s$ and $E_i$ are...
quasilinear, quite similar to that of $E_g$. Figure 3(d) presents the spatial profiles of $n(z)$, $p(z)$, and $n_i(z)$. We note that $n_i$ varies linearly with $z$ such that it is small where $E_g$ is large and vice versa.

Spatial profiles of $G(z)$ and $R(n, p; z)$ are provided in figure 3(e). The generation rate is higher near the front face and lower near the rear face of the CZTSSe layer, which is in accord with the understanding [38, 70] that more charge carriers are generated in regions where $E_g$ is lower and vice versa; less energy is required to excite a charge carrier from the valence band to the conduction band when $E_g$ is lower. The $J_{dev} – V_{ext}$ curve of the solar cell is shown in figure 3(f). From this figure, $J_{dev} = 32.11$ mA cm$^{-2}$, $V_{ext} = 0.53$ V, and FF = 74.0% for best performance.

3.7. Optimal solar cell: sinusoidally graded bandgap and planar/periodically corrugated backreflector

Finally, we considered the maximization of $\eta$ for solar cells with a sinusoidally graded CZTSSe layer according to equation (4) and a periodically corrugated backreflector. The parameter space used for optimizing $\eta$ is:

$$L_s \in [100, 2200]$ nm, $E_{g,\text{min}} \in [0.91, 1.49]$ eV, $A \in [0, 1]$, $\alpha \in [0, 8]$, $K \in [0, 8]$, $\psi \in [0, 1]$, $L_g \in [1, 550]$ nm, $\zeta \in (0, 1)$, and $L_x \in [100, 1000]$ nm. The values of $J_{dev}$, $V_{ext}$, FF, and $\eta$ predicted by the coupled optoelectronic model are presented in table 8 for eight representative values of $L_s$. The values of $E_{g,\text{min}}, A, K, \alpha, \psi, L_g, \zeta$, and $L_x$ for the optimal designs are also provided in the same table. For comparison, the corresponding data for optimal solar cells with a planar backreflector ($L_g = 0$) are provided in table 9.

Just as in sections 3.5 and 3.6.2, on comparing tables 8 and 9, we found that periodic corrugation of the Mo backreflector slightly improves $\eta$ for $L_s \lesssim 600$ nm. For $L_s = 200$ nm, the optimal efficiency predicted is
Table 8. Predicted parameters of the optimal CZTSe solar cell with a specified value of \( L_s = 100, 2200 \text{ nm} \), when the CZTSe layer is sinusoidally graded \((A = 0)\) according to equation (4) and the Mo backreflector is periodically corrugated. The values of \( E_{g, \text{min}} \) provided pertain to the optical part of the model.

| \( L_s \) (nm) | \( E_{g, \text{min}} \) (eV) | \( A \) | \( K \) | \( \alpha \) | \( \psi \) | \( L_g \) (nm) | \( \zeta \) | \( I_{oc} \) (mA cm\(^{-2}\)) | \( V_{oc} \) (V) | \( FF \) (%) | \( \eta \) (%) |
|--------------|----------------|-------|-------|-------|-------|---------|-----|--------------|----------|--------|--------|
| 100          | 0.92           | 0.98  | 3     | 6     | 0.75  | 100     | 0.50 | 500          | 25.72    | 701    | 78.7   | 14.22   |
| 200          | 0.92           | 0.99  | 3     | 6     | 0.75  | 100     | 0.51  | 510          | 32.99    | 716    | 77.5   | 17.83   |
| 300          | 0.92           | 0.98  | 2     | 6     | 0.75  | 100     | 0.51  | 510          | 35.15    | 745    | 74.7   | 19.58   |
| 400          | 0.92           | 0.98  | 2     | 6     | 0.75  | 100     | 0.51  | 510          | 36.32    | 762    | 74.4   | 20.62   |
| 600          | 0.92           | 0.98  | 2     | 6     | 0.75  | 100     | 0.50  | 500          | 37.23    | 771    | 74.8   | 21.47   |
| 870          | 0.92           | 0.98  | 2     | 6     | 0.75  | 100     | 0.50  | 500          | 37.39    | 772    | 75.2   | 21.74   |
| 1200         | 0.92           | 0.98  | 2     | 6     | 0.75  | 100     | 0.51  | 510          | 37.08    | 766    | 74.8   | 21.26   |
| 2200         | 0.92           | 0.98  | 2     | 6     | 0.75  | 100     | 0.51  | 510          | 36.45    | 736    | 72.8   | 19.56   |

Table 9. Predicted parameters of the optimal CZTSe solar cell with a specified value of \( L_s = 100, 2200 \text{ nm} \), when the CZTSe layer is sinusoidally graded \((A = 0)\) according to equation (4) and the Mo backreflector is planar \((L_g = 0)\). The values of \( E_{g, \text{min}} \) provided pertain to the optical part of the model.

| \( L_s \) (nm) | \( E_{g, \text{min}} \) (eV) | \( A \) | \( K \) | \( \alpha \) | \( \psi \) | \( J_{sc} \) (mA cm\(^{-2}\)) | \( \eta \) (%) |
|--------------|----------------|-------|-------|-------|-------|-----------------|--------|
| 100          | 0.91           | 0.99  | 3     | 6     | 0.75  | 25.65           | 703    | 78.6   | 14.19   |
| 200          | 0.92           | 0.99  | 3     | 6     | 0.75  | 32.40           | 719    | 75.0   | 17.48   |
| 300          | 0.92           | 0.98  | 2     | 6     | 0.75  | 33.94           | 744    | 75.0   | 19.01   |
| 400          | 0.92           | 0.98  | 2     | 6     | 0.75  | 35.69           | 762    | 75.0   | 20.35   |
| 600          | 0.92           | 0.98  | 2     | 6     | 0.75  | 37.17           | 771    | 74.8   | 21.46   |
| 870          | 0.92           | 0.98  | 2     | 6     | 0.75  | 37.39           | 772    | 75.2   | 21.74   |
| 1200         | 0.92           | 0.98  | 2     | 6     | 0.75  | 37.08           | 766    | 74.8   | 21.26   |
| 2200         | 0.92           | 0.98  | 2     | 6     | 0.75  | 36.45           | 736    | 72.8   | 19.56   |

17.48% with a planar backreflector (table 9) and 17.83% with a periodically corrugated backreflector (table 8). The optimal bandgap parameters for either backreflector are: \( E_{g, \text{min}} = 0.92 \text{ eV} \), \( A = 0.99 \), \( \alpha = 6 \), \( K = 3 \), and \( \psi = 0.75 \). The geometric parameters of the optimal periodically corrugated backreflector are: \( L_g = 100 \text{ nm}, \zeta = 0.51 \), and \( L_s = 510 \text{ nm} \). For \( L_s = 2200 \text{ nm} \), the optimal efficiency predicted is 19.56%, regardless of the geometry of the backreflector, the optimal bandgap parameters being: \( E_{g, \text{min}} = 0.92 \text{ eV} \), \( A = 0.98 \), \( \alpha = 6 \), \( K = 2 \), and \( \psi = 0.75 \). Indeed, the effect of periodic corrugation remains the same as in the cases of the homogeneous bandgap (section 3.5) and the linearly graded bandgap (section 3.6.2): very small improvement for thin CZTSe layers and no improvement beyond \( L_s \approx 600 \text{ nm} \).

The optimal designs in table 8 have \( L_g \in [100, 110] \text{ nm}, \zeta \in [0.5, 0.51] \) and \( L_s \in [500, 510] \text{ nm} \). The values of \( E_{g, \text{min}} \in [0.91, 0.92] \text{ eV}, A \in [0.98, 0.99], \alpha = 6, \psi = 0.75, \) and \( K \in \{2, 3\} \) for both planar and periodically corrugated backreflectors.

The highest efficiency achievable is predicted to be 21.74% with a sinusoidally graded CZTSSe layer of thickness \( L_s = 870 \text{ nm} \), whether the backreflector is planar (table 9) or periodically corrugated (table 8). Figure 4 shows the projections of the nine-dimensional space onto the sets of axes with the efficiency on the vertical axis and each of the optimization parameters on the horizontal axis, when \( L_s = 870 \text{ nm} \) and the backreflector is periodically corrugated. The large dots highlight the location of the solar cell with the maximum efficiency. The optimal combination of the values of the parameters \( E_{g, \text{min}}, A, \alpha, K, \psi, L_g, \zeta \), and \( L_s \) is recorded in table 8.

The highest possible efficiency (21.74%) with a sinusoidally graded CZTSSe layer amounts to a relative increase of 83.6% over the optimal efficiency of 11.84% with a homogeneous CZTSSe layer of thickness \( L_s = 1200 \text{ nm} \) (sections 3.4 and 3.5). Along with the increase in efficiency, \( J_{sc} \) increases from 30.13 to 37.39 mA cm\(^{-2}\) (a relative increase of 24.0%), \( V_{oc} \) from 558 to 772 mV (a relative increase of 38.3%), and FF from 70.3% to 75.2% (a relative increase of 6.9%).

The highest possible efficiency (21.74%) with a sinusoidally graded CZTSSe layer is 27.3% higher than the highest possible efficiency (17.07%) with a linearly graded CZTSSe layer (section 3.6.2). The short-circuit current density for sinusoidal grading is somewhat higher as well, but the open-circuit voltage is enhanced considerably from 628 mV to 772 mV. Let us note, however, that the optimal sinusoidally graded CZTSSe layer is only 870 nm thick, but its optimal linearly graded counterpart is 2200 nm thick. Indeed, the sinusoidally graded bandgap is more efficient than the homogeneous and linearly graded bandgaps for all considered thicknesses of the CZTSSe layer.
The variations of $E_g$ and $\chi$ with $z$ in the semiconductor region of the solar cell with the optimal sinusoidally graded 870 nm thick CZTSSe layer are provided in figures 5(a), (b). With $E_{g,\min} = 0.92$ eV and $A = 0.98$, $E_g(z) \in [0.92, 1.486]$ eV. The magnitude of $E_g(z)$ is large near both faces of the CZTSSe layer, which elevates $V_{oc}$ [28]. Furthermore, bandgap grading in the proximity of the rear face of the CZTSSe layer keeps the minority carriers away from that face (where recombination would be highly favored in the absence of the $Al_2O_3$ layer.)
to reduce recombination [71] and improve the carrier collection due to the drift field provided by the bandgap grading [72]. The regions in which $E_g$ is small are of substantial thickness, and it is those very regions that are responsible for increasing the electron-hole-pair generation rate [38, 70], because less energy is required to excite an electron-hole pair across a narrower bandgap. Thus, this bandgap profile is ideal for the enhancement of $V_{oc}$ while maintaining a large $J_{sc}$.

Figure 5 shows the variations of $E_c, E_v, \chi, E_e, E_i, E_s, n(z), p(z), n_i(z)$, and $E_g$ and $E_i$ in the semiconductor region of the optimal solar cell with the 870 nm thick CZTSSe layer with sinusoidally graded bandgap. (f) $J_{dev}-V_{ext}$ and $P-V_{ext}$ curves of this solar cell. The numerical values of $J_{dev}$ and $V_{ext}$ for maximum $P$ are also identified. The spatial profiles are the same whether the Mo backreflector is periodically corrugated (table 8) or planar (table 9).

### 4. Concluding remarks

We implemented a coupled optoelectronic model along with the differential evolution algorithm to assess the efficacy of grading the bandgap of the CZTSSe layer for enhancing the power conversion efficiency of thin-film CZTSSe solar cells. Both linearly and sinusoidally graded bandgaps were examined, with the Mo backreflector in the solar cell being either planar or periodically corrugated.

An 870 nm thick sinusoidally graded CZTSSe layer accompanied by a periodically corrugated backreflector delivers a 21.74% efficiency, 37.39 mA cm$^{-2}$ short-circuit current density, 772 mV open-circuit voltage, and 75.2% fill factor. Even if the backreflector is flattened, these quantities do not alter. In comparison, $\eta = 11.84\%$, $J_{sc} = 31.13$ mA cm$^{-2}$, $V_{oc} = 558$ mV, and FF = 70.3%, when the bandgap is homogeneous and the
backreflector is planar. Efficiency can also be enhanced by linearly grading the bandgap, but the gain is smaller compared to the case of sinusoidal bandgap grading.

The generation rate is higher in the broad small-bandgap regions than elsewhere in the CZTSSe layer, when the bandgap is sinusoidally graded. Since the bandgap is high close to both faces of the CZTSSe layer, $V_{oc}$ is high in the optimal designs [20, 28]. Both of these features are responsible of enhancing $\eta$.

The placement of an ultrathin $\text{Al}_2\text{O}_3$ layer behind the rear face of the CZTSSe layer helps remove an unwanted $\text{Mo}(\text{S}_\xi\text{Se}_{1-\xi})_2$ layer and slightly enhances the efficiency. Furthermore, for a thin CZTSSe layer ($L_s \leq 500$ nm), periodically corrugating the backreflector can also provide small gains over a planar backreflector.

Optoelectronic optimization thus indicates that 21.74% efficiency can be achieved for CZTSSe solar cell with a 870 nm thick CZTSSe layer. This efficiency significantly higher compared to 12.6% efficiency demonstrated with CZTSSe layers that are more than two times thicker. Efficiency enhancements of comparable magnitude—e.g. 22% to 27.7%—have been predicted by bandgap grading of the CIGS layer in thin-film CIGS solar cells [26] (which, however, use some materials that are not known to be abundant on Earth). Thus, bandgap grading can provide a way to realize more efficient thin-film solar cells for ubiquitous small-scale harnessing of solar energy.

Acknowledgments

The authors thank anonymous reviewers for invaluable suggestions to improve the contents of this paper. A Lakhtakia acknowledges the Charles Godfrey Binder Endowment at the Pennsylvania State University and the Otto Mønsted Foundation in Frederiksberg, Denmark for partial support. The research of F Ahmed and A Lakhtakia was partially supported by US National Science Foundation (NSF) under grant number DMS-1619901. The research of TH Anderson and PB Monk was partially supported by the US National Science Foundation (NSF) under grant number DMS-1619904.

Appendix. Relative permittivities of materials in the optical regime

Spectra of the real and imaginary parts of the relative permittivity $\varepsilon(\lambda_0)/\varepsilon_0$ of MgF$_2$ [52], AZO [53], od-ZnO [54], Cds [56], Mo [57], and Al$_2$O$_3$ [59] in the optical regime are displayed in figure A1. Spectra of the real and imaginary parts of the relative permittivity of CZTS and CZTSe are available [6]. These were incorporated in an energy-shift model [36, 73] to obtain the relative permittivity of CZTSSe as a function of $\xi$ (and, therefore, the bandgap $E_g$) and $\lambda_0$ in the optical regime, as shown in figure A2. Spectra of the real and imaginary parts of the
Relative permittivity of MoS$_2$ and MoSe$_2$ are available for $\lambda_0 \leq 1240$ nm [67]. These were first linearly extrapolated for $\lambda_0 \in (1240, 1400]$ nm and then incorporated in the energy-shift model [36, 73] to obtain the relative permittivity of Mo(S$_2$Se$_{1-\xi}$)$_2$ as a function of $\xi$ and $\lambda_0$, as shown in figure A3.

Figure A2. (a) Spectrums of Re [$\varepsilon$/$\varepsilon_0$] and Im [$\varepsilon$/$\varepsilon_0$] of CZTS and CZTSe, (b) Re [$\varepsilon$/$\varepsilon_0$] and (c) Im [$\varepsilon$/$\varepsilon_0$] of CZTSSe as functions of $\lambda_0$ and $\xi$.

Figure A3. (a) Spectrums of Re [$\varepsilon$/$\varepsilon_0$] and Im [$\varepsilon$/$\varepsilon_0$] of MoS$_2$ and MoSe$_2$, (b) Re [$\varepsilon$/$\varepsilon_0$] and (c) Im [$\varepsilon$/$\varepsilon_0$] of Mo(S$_2$Se$_{1-\xi}$)$_2$ as functions of $\lambda_0$ and $\xi$.
ORCID iDs

Akhlesh Lakhtakia  https://orcid.org/0000-0002-2179-2313

References

[1] Singh R, Alapatt G F and Lakhtakia A 2013 IEEE J. Electron. Dev. Soc. 1 1129–44
[2] Dudley D 2019 Renewable Energy Costs Take Another Tumble, Making Fossil Fuels Look More Expensive Than Ever https://www.forbes.com/sites/dominicdudley/2019/05/29/renewable-energy-costs-tumble/?sh=4a02b4e (Accessed 05 July 2019)
[3] Singh R, Alapatt G F and Bedi G 2014 Folia Univ.: Electron. Energ. 27 275–98
[4] Lee T D and Ebborg A U 2017 Renew. Sustain. Energy Rev. 70 1286–97
[5] Candelise C, Winkel M and Gross R 2012 Prog. Photovolt.: Res. Appl. 20 816–31
[6] Adachi S 2015 Earth-Abundant Materials for Solar Cells: Cu2-II-VI Semiconductors (Chichester: Wiley)
[7] Wang W, Winkler M T, Gunawan O, Gokmen T, Todorov T K, Zhu Y and Mitzi D B 2014 Adv. Energy Mater. 4 1301465
[8] Wong I H, Zakutayev A, Major J D, Hao X, Walsh A, Todorov T K and Saucedo E 2019 J. Phys. 10312001
[9] Jackson P, Wuerz R, Hariskos D, Lotter E, Witte W and Powalla M 2016 Phys. Status. Solidi. Solid. 10.583–6
[10] Green M A, Hishikawa Y, Dunlop E D, Levi D H, Hoehl-Ebininger I and Ho-Bailie A W Y 2018 Prog. Photovolt.: Res. Appl. 26 427–36
[11] Gershon T, Gokmen T, Gunawan O, Haught R, Guha Sand Shin B 2014 MRS Commun. 11 159–70
[12] Kanevce A, Repins I and Wei S H 2015 Sol. Energy Mater. Sol. Cells 133 119–25
[13] Lee Y S, Gershon T, Gunawan O, Todorov T K, Gokman T, Virgus Y and Guha S 2015 Adv. Energy Mater. 5 1401372
[14] Gokman T, Gunawan O, Todorov T K and Mitzi D B 2013 Appl. Phys. Lett. 103 105306
[15] Frisk C, Ericson T, Li S Y, Szaniawski P, Olsson J and Platzter-Bjorkman C 2016 Sol. Energy Mater. Sol. Cells 144 364–70
[16] Repins I et al. 2013 J. Appl. Phys. 114 043507
[17] Gunawan O, Todorov T K and Mitzi D B 2010 Appl. Phys. Lett. 97 233506
[18] Gokmen T, Gunawan O and Mitzi D B 2013 J. Appl. Phys. 114 114511
[19] Mitzi D B, Gunawan O, Todorov T K, Wang K and Guha S 2011 Sol. Energy Mater. Sol. Cells 95 1421–36
[20] Gloclecker M and Sites JR 2005 J. Appl. Phys. 98 103703
[21] Schmid M 2017 Semicond. Sci. Technol. 32 043003
[22] van Lare C, Yin G, Polman A and Schmid M 2015 ACS Nano 9 6903–13
[23] Goffard J, Colin C, Mollica F, Cattoni A, Sauvan C, Lalanne P, Guilleminoles J-F, Naghavi N and Collin S 2017 IEEE J. Photovolt. 7 1433–41
[24] Vernarging B, Wütjen J T, Füllstörn V, Rostvall F, Edoff M, Kotipalli R, Henry F and Flandre D 2014 Prog. Photovolt.: Res. Appl. 22 10123–9
[25] Ahmad F, Anderson T H, Monk P B and Lakhtakia A 2018 Proc. SPIE 10733 107310L
[26] Ahmad F, Anderson T H, Monk P B and Lakhtakia A 2019 Proc. SPIE 10568 6078–76
[27] Woo K, Kim Y, Yang W, Kim K, Kim I, Oh Y, Kim J Y and Moon J 2013 Sci. Rep. 3 03069
[28] Yang K-J et al. 2016 J. Mater. Chem. A 4 10151
[29] Hwang D-K, Ko B-S, Jeon D-H, Kang K-J, Sung S-J, Yang K-J, Nam D, Cho S, Cheong H and Kim D-H 2017 Sol. Energy Mater. Sol. Cells 161 162–9
[30] Ferhat H and Djefal F 2018 Opt. Mater. 76 393–9
[31] Mohammadnejad S and Parashkhon A B 2017 Appl. Phys. A 123 758
[32] Hiromiwa D, Murata M, Ashida N, Tazawa Y and Minemoto T 2014 J. Appl. Phys. J. Phys. 53 071201
[33] Simya O K, Mahabobratcha A and Balachander K 2016 Superlattices Microstruct. 92 285–93
[34] Chadal M, Chadal A, Bouzaki M M, Alleriere M, Benyoussef B and Charles J-P 2017 Mater. Res. Express 4 115503
[35] Bag S, Gunawan O, Gokmen T, Zhu Y, Todorov T K and Mitzi D B 2012 Energy Environ. Sci. 5 7060
[36] Nakane A, Tampo H, Tamakoshi M, Fujimoto S, Kim K M, Kim S, Shibata H, Nikif S and Fujitawa H 2016 J. Appl. Phys. 120 064505
[37] Burgelman M and Marleijn J 2008 Proc. 23rd European Photovoltaic Solar Cell Energy Conf. (Valencia, Spain, 1-5 September) pp 2151–5
[38] Forsahl S 2010 Solar Cell Device Physics 2nd edn (Burlington, MA: Academic)
[39] Anderson T H, Cavelli B T, Monk P B and Lakhtakia A 2020 J. Comput. Phys. 407 109242
[40] Glysis K N and Gaylord T K 2013 J. Opt. Soc. Am. A 28 2061–80
[41] Poli J A, Jr, Mackay T G and Lakhtakia A 2013 Electromagnetic Surface Waves: A Modern Perspective (Walsham, MA: Elsevier)
[42] National Renewable Energy Laboratory, Reference Solar Spectral Irradiance: Air Mass 1.5 http://rredc.nrel.gov/solar/spectra/am1.5/ (Accessed 05 June 2019)
[43] Nelson J 2003 The Physics of Solar Cells (London: Imperial College Press)
[44] Lehrenfeld C 2010 Hybrid discontinuous Galerkin methods for solving incompressible flow problems Diplom Ingenieur Thesis Rheinisch-Westfalischen Technischen Hochschule Aachen
[45] Cockburn B, Gopalakrishnan J and Lazarov R 2009 SIAM J. Numer. Anal. 47 1319–65
[46] Fu Q, Qiu W and Zhang W 2015 ESAIM: Math. Model. Numer. Anal. 49 225–56
[47] Brinkman D, Fellner K, Markowich P and Wolfram M T 2013 Math. Models Methods Appl. Sci. 23 839–72
[48] Liu F et al. 2017 NPG Asia Mater 9 e401
[49] Storn R and Price K 1997 J. Glob. Optim. 11 341–59
[50] Song J, Li S S, Huang C H, Crisalle O D and Anderson T J 2004 Solar-State Electron 48 73–9
[51] Rajan G, Aryal C, Ashrafeh T, Kariki S, Idbah A R, Ranjan V, Collins R W and Marsillach S 2015 Proc. 42nd IEEE Photovoltaics Specialist Conf. (New Orleans, LA, 14–19 June)
[52] Dodge M J 1984 Appl. Opt. 23 1980–5
[53] Ehrmann N and Reinecke-Koch R 2010 Thin Solid Films 519 1475–85
[54] Stelling C, Singh C R, Karg M, König T A F, Thelakkat M and Retsch M 2017 Sci. Rep. 7 42530
[55] Welling IS J, Samantilake A P, Warren P, Heavens S N and Dharmadasa I M 2008 Semicond. Sci. Technol. 23 125003
[56] Trehanare R E, Seymour-Pierce A, Durose K, Huchings K, Roncallos S and Lane D 2011 J. Phys.: Conf. Ser. 268 012038
[57] Query M R 1987 Contractor Report CRDEC–CR–88009 University of Missouri, Kansas City https://apps.dtic.mil/dtic/tr/fulltext/u2/a192210.pdf (Accessed 08 July 2019)
[58] Iskander M F 2012 Electromagnetic Fields and Waves (Hong Kong, IL: Waveland Press)
[59] Boidin R, Halenkovitch F, Nazabal V, Benei L and Némeč P 2016 Ceram. Int. 42 1177–82
[60] Martín-Palma R J and Lakhtakia A 2010 Nanotechnology: A Crash Course (Bellingham, WA: SPIE)
[61] Wei H, Ye Z, Li M, Su Y, Yang Z and Zhang Y 2017 CrystEngComm 13 2222
[62] Ahmad F, Anderson T H, Civiletti B J, Monk P B and Lakhtakia A 2018 J. Nanophotonics 12 016017
[63] Anderson T H, Monk P B and Lakhtakia A 2018 J. Photonics Energy 8 034501
[64] Chen Y, Kivisaari P, Pistol M E and Anttu N 2016 Nanotechnology 27 435404
[65] Brezzi F, Marini I D, Micheletti S, Pietra P, Sacco R and Wang S 2005 Handbook of Numerical Analysis: Numerical Methods for Electrodynamic Problems ed W H A Schilders and E J W ter Maten (Amsterdam: Elsevier) pp 317–441
[66] Frisk C, Platzer-Björkman C, Olsson J, Szaniawski P, Wätjen J T, Fjällström V, Salomé P and Edoff M 2014 J. Phys. D: Appl. Phys. 47 485104
[67] Beal A R and Hughes H P 1979 J. Phys. C: Solid State Phys. 12 881–90
[68] Gokmen T, Gunawan O and Mitzi D B 2014 Appl. Phys. Lett. 105 033903
[69] Shockley W and Queisser H J 1961 J. Appl. Phys. 32 510–9
[70] Repins I et al 2016 Proc. 43rd IEEE Photovoltacs Specialist Conf. (Portland, OR, 3–10 June) pp 309–14
[71] Dullweber T, Lundberg O, Malmström J, Bodegard M, Stolt L, Rau U, Schock H W and Werner J H 2001 Thin Solid Films 387 11–3
[72] Hutchby J A 1975 Appl. Phys. Lett. 26 457–9
[73] Hirate Y, Tampo H, Minoura S, Kadowaki H, Nakane A, Kim K M, Shibata H, Niki S and Fujiwara H 2015 J. Appl. Phys. 117 015702