

Atomistic modeling of energy band alignment in CdSeTe surfaces

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Abstract

Atomistic modeling based on Density Functional Theory (DFT)- 1/2 method coupled with surface Green's function has been employed to investigate the energy band alignment results in cadmium selenium telluride (CdSeTe) surfaces. The structural and electronic properties of the bulk ternary alloy were established before cleaving the CdSeTe low index surface facets. The dependency of atomic-scale electronic features on different plane orientations was explored by studying the energy band alignment diagrams in the unreconstructed and reconstructed surfaces. While the low index CdSeTe surface geometry reconstructions replicate the CdTe surface geometries, the energy band alignment features of the unreconstructed and reconstructed CdSeTe surfaces differ from those observed in CdTe low index surfaces. The structurally relaxed reconstructed CdSeTe surface results in purely flat bands as opposed to an internal cusp feature observed in CdTe surfaces. The presence of an internal energy cusp in CdTe(111) surfaces is expected to play a key role in enhancing the hole charge transport towards the back of CdTe-only solar cell device and the absence of such feature in CdSeTe surface may explain one of the reason for the lower performance of CdSeTe-only solar cell seen experimentally.

Keywords: Cadmium selenium telluride, ternary alloy, Density functional theory, Energy band alignment

1. Introduction

Cadmium telluride (CdTe) solar cells over the past few years have emerged as a key technology in thin-film photovoltaics (PV) market. The efficiency improvement from 16.7% to 22.1% over seven years has enabled the cost of CdTe PV electricity generation to be lower than both fossil fuel and silicon PV based electricity[1, 2, 3]. Cadmium toxicity often considered to be an issue with CdTe photovoltaics has been explained as not being a limiting factor under various studies[4, 5, 6]. Previous studies have demonstrated efficiencies of 18% with thin-film CdTe-only absorber material fabricated using a sublimation process[7]. The recent increase in the device efficiency to 22.1% has been realized through alloying selenium (Se) within the CdTe absorber layer[8]. Alloying Se to the CdTe creates a ternary CdSe_xTe_{1-x} (CdSeTe) alloy, which in the zinc blende phase has a lower bandgap than CdTe[1, 9, 10]. It has been shown that efficiencies over 19% could be achieved in the solar cells fabricated with CdTe at the back of CdSeTe absorber layer[11]. Published literature indicates that the lower bandgap CdSeTe semiconductor ternary alloy increases the device short-circuit current by improving the absorption in the long wavelength spectrum[12, 10].

In the case of CdTe-only absorber based solar cell, research studies suggest that CdTe surface characteristics govern the minority carrier lifetime that determines the CdTe device performance[13]. The non-polar and polar low index CdTe surface facets have been extensively investigated using theoretical and experimental techniques to understand the relaxation and reconstruction of the CdTe surfaces[14, 15, 16]. Theoretical analyses based on Density Functional Theory (DFT) have also been used to probe the surface energy band

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alignment of the unreconstructed and reconstructed CdTe surfaces[17]. *Nicholson et. al.* in different DFT studies further observed that a cusp feature developed in CdTe(111) surface energy band alignment is retained for the CdTe/Te interface and attributed that cusp feature as an additional mechanism for hole charge transport towards the back electrode[17, 18]. The above observations imply the importance of understanding the surface behavior for predicting the interface properties in heterojunction solar cells.

However, the geometrical and electronic behavior of CdSeTe ternary alloys have not been explored hitherto. It has been observed experimentally that the CdTe-only absorber based solar cell is a low performing device in comparison to CdSeTe/CdTe absorber based solar cells[11, 19, 20]. This shows that CdSeTe surface forming distinct interface would influence the electronic properties in the solar cell device performance. A comprehensive understanding of the electronic properties of CdSeTe surface is therefore essential for further improvement in the device performance.

In past, plane wave basis set approach has been used to calculate surface properties using the slab model. In the slab model, the constructed supercell is finite in the direction perpendicular to the surface facet of interest. As a result, different surface properties such as surface energies, electrostatic potential and work functions of the slab would be altered due to the quantum confinement along the surface direction[21, 22, 23]. In another research, *Martsinovich et. al.* showed that converging the surface electronic properties depends on the slab thickness and could be cumbersome with respect to the system size[24].

To overcome the challenges posed by the slab model, Surface Green's function (SGF) has been utilized as an alternative means for the surface modeling[25, 26, 27]. The one probe model shown in Fig.3 employs the SGF formulation by dividing the semi-infinite system into a finite surface region coupled to a semi-infinite bulk region acting as the source of infinite electrons. The surface region interacts with the infinite reservoir of electrons leading to better charge distribution in the surface region and charge transfer between surface and bulk material, thus accounting for accurate surface electronic properties[23].

In this work, we utilize atomistic modeling based on DFT coupled with surface Green's function to study the geometrical and electronic features of polar Cd-terminated low index CdSeTe(100), (111), and non-polar CdSeTe(110) surfaces. Since CdSeTe is a group II-VI based compound alloy, similar reconstruction effects on CdSeTe surface were expected as observed in CdTe surface experimentally. Thus both the unreconstructed and reconstructed CdSeTe surfaces were simulated to evaluate the energy band alignment characteristics for each case. We also report the experimental device performance of CdSeTe-only and CdTe-only devices fabricated under identical conditions. The energy band alignment diagrams for the CdSeTe and CdTe surface comparison at equilibrium were plotted to understand the charge transport within CdSeTe-only and CdTe-only absorber based solar cells. The comparison also give insights into the potential reason for (but not limited to) the lower performance of CdSeTe-only absorber based solar cells.

2. Experimental and Computational details

2.1. Experimental methods

Photovoltaic devices with two p-type absorbers were fabricated using similar processing conditions and optimized for high device performance. The devices were fabricated on NSG Pilkington TEC10 soda lime glass that had a layer of fluorine doped tin oxide deposited by the manufacturer as the n-type transparent conducting oxide. Both the substrates had a 100 nm layer of $\text{MgZn}_{1-x}\text{O}_x$ ($x=11$ at.%) (MZO) deposited by RF sputter deposition using a single $\text{MgZn}_{1-x}\text{O}_x$ target. Thereafter, the absorber deposition and CdCl_2 passivation treatment were performed using an in-line sublimation system with 9 processing stations designed and optimized for fabrication of CdTe-based thin-film PV devices. This system is extensively described by Swanson et al[28]. The first substrate was heated to a temperature of about 615°C and the substrate was then transferred to the CdTe sublimation station using a computer controlled magnetic transfer mechanism. About 3 μm of CdTe was deposited on the preheated substrate over 150 seconds following which the substrate was transferred to CdCl_2 sublimation station for 200 seconds. The substrate was then moved to an annealing station for 200 seconds. CdCl_2 was deposited at 442°C and annealing station operated at 400°C. Thereafter the substrate was transferred to a cooling station within the vacuum chamber for 300 seconds before it was removed from the vacuum chamber and the residual CdCl_2 film from the surface was rinsed off using deionized water and dried using pressurized ultrahigh purity nitrogen gas.

For the CdSeTe device, the same fabrication system was used. However, the processing conditions were slightly different as they were optimized for deposition of a lower band gap material with a deposition rate different from the CdTe. The substrate with 100 nm of MZO was preheated to a temperature of about 538°C after which the substrate was transferred to the station containing a CdSe_xTe_{1-x} ($x=20$) source charge. A 3.3 μ m film was deposited over 360 seconds with the CdSeTe sublimation source operating at 575°C. Following the deposition of the film, the substrate was transferred to the CdCl₂ passivation treatment station where the film was exposed to CdCl₂ vapor for 900 seconds from a CdCl₂ sublimation source operating at a temperature of 450°C. Thereafter, the substrate was cooled in the vacuum chamber for 180 seconds. The substrate was removed and like the earlier CdTe film, the residual CdCl₂ layer was rinsed off using deionized water and dried using a pressurized ultrahigh purity nitrogen gas. The high purity CdTe, CdSeTe and CdCl₂ materials used in this study were provided by 5N Plus Inc.

Following this the films were moved to an evaporator where 30 nm of pure Te was vapor deposited. The substrates were then painted with graphite and nickel paint in polymer binder manufactured by Henkel Chemicals Company that formed the back electrodes. The films were masked and delineated into square area devices (area ~ 0.65 cm²) using a plastic abrasion medium sprayed using pressurized gas. 25 small area research devices were fabricated for substrate with CdTe film while 10 devices were fabricated on the substrate with CdSeTe film. It must be noted that the substrates used for both the device structures were identical. However, half of the CdSeTe substrate did not receive the 30 nm Te layer and therefore only the films with Te back-contact layer are eligible for comparison with the CdTe devices that are discussed here.

Electrical measurements were performed with a Model 10600 solar simulator from ABET Technologies using a high-pressure xenon arc lamp with an AM1.5 filter. Current density vs voltage curves were generated based on electrical measurements performed using Keithley 2420 SourceMeter controlled via LabView. Current-density and device area for each set of measurement were calibrated to cells measured by National Renewable Energy Laboratory (NREL). Device areas were measured using a webcam that took an image of a backlit solar cell and counted the pixels below a certain brightness.

The box plot (see Fig. 10) shows the % efficiency and % Fill Factor comparison for the CdTe-only and CdSeTe-only absorber based solar cell devices. CdTe-only devices consistently showed higher efficiencies and the fill factor values with a tight spread in comparison to the CdSeTe-only devices. The larger spread in the CdSeTe-only devices could be attributed to the variation in thickness during the CdSeTe film deposition. Out of several devices, Fig. 10(c) shows the current density vs voltage curve for the highest performing device from each experiment set. The lower performance seen in CdSeTe-only devices is explained further using DFT-based atomistic modeling.

2.2. Computational details

The DFT CdSeTe bulk and surface models were simulated using the QuantumATK P-2019.03 software tool[29]. The single particle Kohn-Sham eigenvalue problem was solved using electronic wavefunctions represented by the Linear Combination of Atomic Orbitals (LCAO) basis scheme. The FHI pseudopotential basis sets for Cd and Se atoms in combination with OpenMX Low (s2p2d1) basis sets[30, 31] for Te atoms were used in all the calculations. The Perdew-Zunger[32] form of the Local Density Approximation (LDA) exchange correlation functional was utilized in the relaxation of the bulk supercells and the surfaces. However, it is well known that DFT underestimates the bandgap values for semiconductors and therefore the semi empirical correction DFT-1/2 method[33] was applied to obtain the appropriate bulk CdSe_xTe_{1-x} bandgap. A Monkhorst-Pack grid with $8 \times 8 \times 8$ k-point sampling was employed for the bulk CdSe_xTe_{1-x} calculations and the density mesh cutoff value was set to 3000 eV.

2.2.1. Bulk cadmium selenium telluride model

Depending on the selenium concentration, cadmium selenium telluride can exist either in the zinc blende or wurtzite phases[10]. The published experimental literature shows a phase transition of CdSe_xTe_{1-x} ($0 < x < 1$) from zinc blende to wurtzite phase between $x = 0.6$ and 0.7 [34]. Therefore, the structural and electronic properties of the bulk CdSe_xTe_{1-x} were investigated using a 16 atom zinc blende and wurtzite supercells (illustrated in fig. 1 a) and fig. 1 b)) for the $x = 0, 0.25, 0.50, \text{ and } 0.75, 1.0$ concentrations

respectively. Depending on the relative Se atomic distance, the ground-state total energy of the above four Se concentrations were calculated for the 16 configurations in total and the lowest energy configuration for each of the concentration was chosen for the further analysis. Three more concentrations of Se $x=0.11$, 0.125 zinc blende and a 16 atom wurtzite supercell for $x=0.875$ were included to verify the credibility of the DFT modeling parameters used in simulation. Se is found to have a high probability for random distribution as a $\text{CdSe}_x\text{Te}_{1-x}$ alloy[35]. To accommodate for the random distribution, the bulk simulations use the special quasirandom structure(SQS) for each of the above described Se concentrations. To generate confidence in the DFT modeling parameters with the SQS generated structures, Se concentration of $x=0.11$ had a 54 atom supercell while $x=0.125$ were calculated with 16,32, and 128 atom zinc blende supercells. It is to be noted that the structural and electronic bandgap values for the $x=0.125$ were close, however we only report the closest match to the literature which came from 128 atom supercell.

Structural properties:. The lattice constants computed for the relaxed $\text{CdSe}_x\text{Te}_{1-x}$ zinc blende and wurtzite phase are tabulated in Table 1. The calculated lattice constants in this study were in good agreement with other theoretical and experimental literature values reported earlier[10, 9]. It was observed that the lattice constant value decreases with an increase in the Se concentration. A good linear fit of the lattice parameters (see fig. 1 c)) indicate that both phases of $\text{CdSe}_x\text{Te}_{1-x}$ alloy follow Vegard's law[10, 36].

Table 1: Lattice constant comparison between DFT LCAO model values calculated in this work, experimental (Exp.) values and other reported theoretical (Theo.) values for respective Se concentrations. The supercell used for $x=0.75$ in reference [9] is double the size of the supercell used in this study) along the c-direction.

Se conc.(x)	Phase	a(Å)	c(Å)	a(Å) Exp.	c(Å) Exp.	a(Å) Theo.	c(Å) Theo.
0	Zinc blende	6.62	-	6.48 ^a , 6.54 ^b	-	6.62 ^c , 6.63 ^d	-
0.125	Zinc blende	6.54	-	-	-	-	-
0.25	Zinc blende	6.48	-	-	-	6.32 ^c	-
0.5	Zinc blende	6.34	-	-	-	6.41 ^c	-
0.75	Wurtzite	4.41	7.23	-	-	4.43 ^c	14.89 ^c
0.875	Wurtzite	4.35	7.08	-	-	-	-
1.0	Wurtzite	4.31	7.01	4.3 ^e	7.01 ^e	4.34 ^c	7.27 ^c

^aRef.[37].

^bRef.[38].

^cRef.[9].

^dRef.[39].

^eRef.[40].

Electronic properties:. For the electronic properties, DFT calculations typically underestimate the band gap values of the CdTe compounds[17]. Therefore, the DFT-1/2 correction scheme[33] was applied to the relaxed $\text{CdSe}_x\text{Te}_{1-x}$ structures to compute the band gap (E_g) values of the zinc blende and the wurtzite phase. Fig.2 shows the bandstructure plot of CdSeTe alloy for various Se content. For the cubic Zinc blende structure the bandgap values decreases with the increase in the Se content. However after transitioning to the wurtzite structure the bandgap values again increases with the Se content. The bandstructure plots confirms that CdSeTe alloys are direct bandgap semiconductor as the conduction band minimum and valence band maximum are located at the center of the Brillouin zone (Γ point). The calculated band gap values are compiled in Table 2 for comparison with the previously reported literature values. The typical band gap bowing feature observed in Se alloyed CdTe compounds was confirmed in fig. 1 d) for the calculated theoretical band gap values. It has been shown previously that the band gap of $\text{CdSe}_x\text{Te}_{1-x}$ alloys could be fitted to a bowing formula[43]:

$$E_g(x) = (1-x)E_g(\text{CdX}) + xE_g(\text{CdY}) - bx(1-x), \quad (1)$$

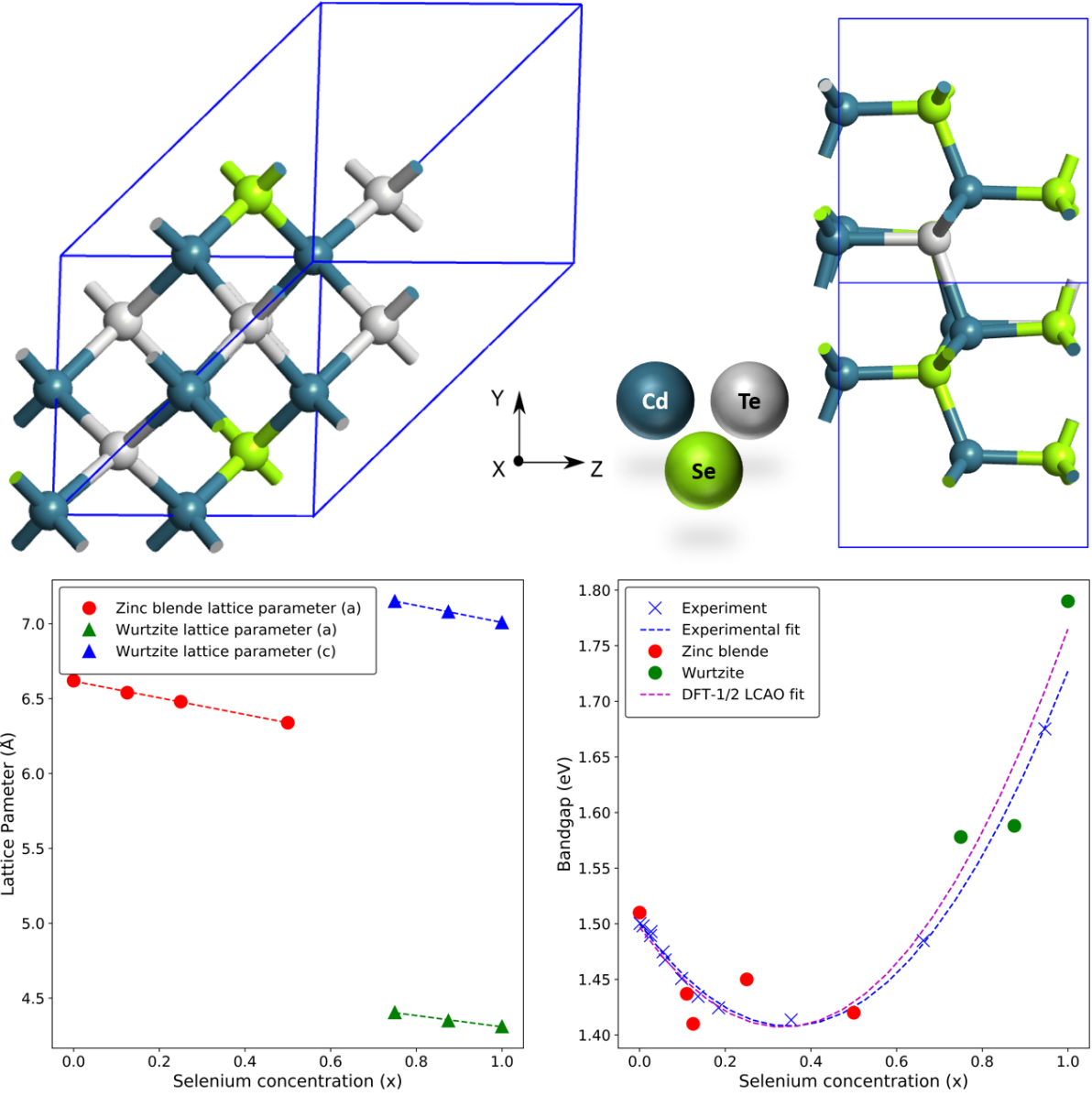


Figure 1: Illustration of a) $\text{CdSe}_{0.25}\text{Te}_{0.75}$ zinc blende phase and b) $\text{CdSe}_{0.75}\text{Te}_{0.25}$ wurtzite phase. c) Calculated lattice parameter of the zinc blende (a) and wurtzite phase (a & c) with respective Se concentration. The linear fit of the lattice parameters indicate the $\text{CdSe}_x\text{Te}_{1-x}$ alloy follow Vegard's law. d) Calculated band gaps vs selenium concentration curve shows the typical bowing feature in $\text{CdSe}_x\text{Te}_{1-x}$ alloy which matches well with the experimental band gap[34].

where b is the "optical bowing coefficient," E_g is the band gap of the alloy at composition x , and $E_g(\text{CdX})$ and $E_g(\text{CdY})$ are the band gap of the binary constituents. A second degree polynomial curve fitting of the experimental and theoretical band gap values was employed to obtain the optical bowing coefficient. The computed bowing parameter $b_{\text{theo}} \sim 0.806$ agrees well with the experimental bowing parameter $b_{\text{exp}} \sim 0.754$ and the published literature[35] values $b_{\text{lit}} \sim 0.8, 0.75$.

Table 2: Band gaps comparison between DFT-only, DFT-1/2 LCAO model values calculated in this work, experimental (Exp.) values and other reported theoretical (Theo.) values for respective Se concentrations.

Se conc.(x)	Phase	E_g (eV) DFT	E_g (eV) DFT-1/2	E_g Exp. (eV)	E_g Theo. (eV)
0	Zinc blende	0.57	1.51	1.50 ^a	1.31 ^b
0.11	Zinc blende	0.46	1.44	-	-
0.125	Zinc blende	0.41	1.41	-	-
0.25	Zinc blende	0.36	1.45	-	1.44 ^b
0.5	Zinc blende	0	1.38	1.48 ^c	1.56 ^b
0.75	Wurtzite	0	1.58	1.425 ^d	1.55 ^b
0.875	Wurtzite	0	1.59	-	-
1.0	Wurtzite	0.32	1.79	1.82 ^e	1.60 ^b

^aRef.[10].

^bRef.[9].

^cRef.[41].

^dRef.[42].

^eRef.[37].

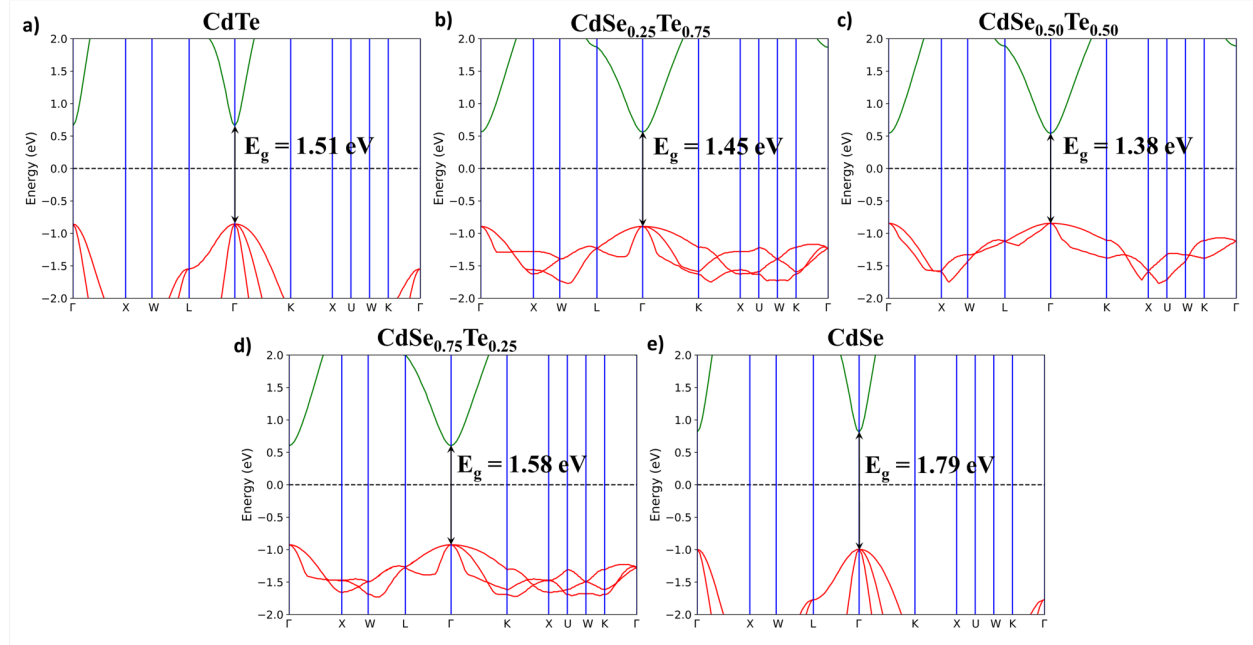


Figure 2: The calculated bandstructure of the zinc blende phase of $\text{CdSe}_x\text{Te}_{1-x}$ for $x=0, 0.25$, and 0.50 and wurtzite phase of the $\text{CdSe}_x\text{Te}_{1-x}$ for $x=0.75, 1.0$. The green line indicates the conduction band minima while the red line depicts the valence band maxima. The dashed line indicates the Fermi level position. The bandstructure calculation was performed using DFT-1/2 correction scheme.

2.2.2. CdSeTe surface model

For bulk $\text{CdSe}_x\text{Te}_{1-x}$ alloy, the electronic properties computed using the DFT LCAO basis set scheme and DFT-1/2 correction method were in good agreement with experimental and other theoretical published literature. Therefore the same modeling parameters were used further to study the energy band alignment features of non-polar CdSeTe(110) as well as polar CdSeTe(100) and (111) surface facets. A one-probe DFT

+ SGF modeling domain (Fig 3) was setup with the CdSeTe bulk electrode region adopting the Dirichlet boundary condition and the surface region adopting Neumann boundary condition for the reasons described by *Nicholson et. al.*[17]. All the low index surface facets were cleaved from bulk CdSe_{0.25}Te_{0.75} (Se at.% = 12.5%) model to closely follow the at. % concentrations (11 at. %) reported in previous studies[1, 20]. A $6 \times 6 \times 150$ Monkhorst-Pack grid distribution of k-points was setup for computing the electronic properties of CdSe_{0.25}Te_{0.75} surface facets.

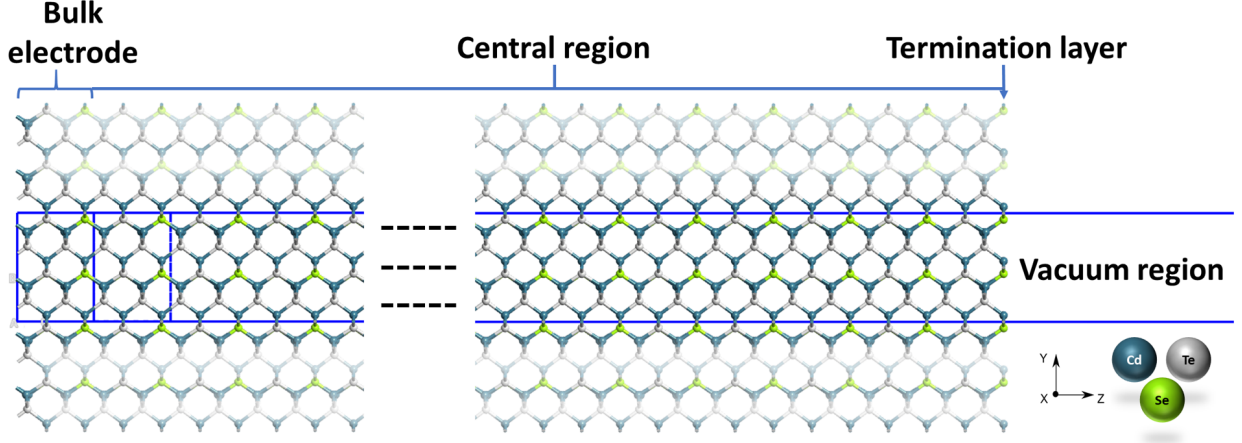


Figure 3: Schematic diagram showing CdSe_{0.25}Te_{0.75}(110) surface one-probe modeling domain.

Six different CdSeTe surfaces were studied to understand the surface properties in various plane orientations. Previous studies have demonstrated the prevalence of (1×1) unreconstructed polar CdTe(100) and CdTe(111) surfaces under certain experimental conditions. Various other DFT studies and films grown under epitaxial conditions have shown that $c(2 \times 2)$ and (2×2) reconstructions in the respective Cd terminated CdTe(100) and CdTe(111) generate thermodynamically stable surface structures[14, 16, 17, 44, 45]. Thus, the four surface configurations described above were evaluated for polar Cd terminated CdSe_{0.25}Te_{0.75} surface facets. The $c(2 \times 2)$ CdSe_{0.25}Te_{0.75}(100) and (2×2) CdSe_{0.25}Te_{0.75}(111) reconstructed surfaces were constructed as per the method described by *Nicholson et. al.*[17]. For the non-polar CdTe(110) surface, earlier DFT studies show that relaxation of the CdTe(110) surface causes atomic chains to tilt[15]. That is why for the CdSeTe(110) surface, structural and electronic properties were compared between non-relaxed and relaxed geometries.

All the unreconstructed and reconstructed CdSe_{0.25}Te_{0.75} facets were structurally relaxed in the central region extending 5-6 nm from the termination surface. A force threshold of 0.05 eV/Å was used in all the surface relaxations[33]. For describing the geometrical features of the relaxed surface, the movement of atoms into and out of the plane of surface atoms with respect to the unrelaxed surface configuration are termed as shrinking/contraction and expansion respectively as has been described before by *Nicholson et. al.* and *Srivastava et. al.*[17, 46]. The electronic properties of the unreconstructed and reconstructed surfaces were compared to gain insight on how reconstructions affect the surface band alignment. Further comparison of the CdSeTe and CdTe surface energy band alignments were performed to understand one of the potential reason for lower performance observed in CdSeTe-only devices.

3. Results and discussion

Cleavage energy γ_c for the CdSe_{0.25}Te_{0.75} surfaces were calculated to verify the stability of the polar and non-polar surfaces. The cleavage energy from the DFT + SGF method was calculated as follows[23]:

$$\gamma_c = \frac{2E_2 - E_1}{2A} \quad (2)$$

where E_2 is the one-probe total energy of the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface, E_1 is the total energy of the two-probe representation of the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ bulk along a given orientation, and A is the cross sectional area of the given simulation domain. The cleavage energy values, γ_c for $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$, (110) , and (111) surfaces were 1.76, 1.05, and 1.37 J/m² respectively. The cleavage energy calculation indicated that non-polar $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface had higher stability than polar $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ followed by $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface and were in qualitatively good agreement with other published literature values[17, 47].

Pertinent electronic features of the low index $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface models were studied to understand the effects of atomic relaxation and surface reconstruction on the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface energy band alignment. Local density of states were computed and projected along the z-direction to generate the energy band alignment plot for all the six surface configurations described earlier. Macroscopically averaged curve fits of the valence band maximum (VBM) and conduction band minimum (CBM) were obtained using the gaussian kernel method described by *Nicholson et. al.*[17]. In accordance with the labels provided in Fig. 4 e), the band gap energy, $E_{\text{CdSe}_{0.25}\text{Te}_{0.75}}^g$ was determined from the energy differences of the VBM and CBM at positions located to closest bulk-like $\text{CdSe}_{0.25}\text{Te}_{0.75}$ structure. The dip observed in the valence band is defined as the surface potential E_{surf} , and was calculated by taking the difference between the curve fit VBM value (labeled point 2) near the surface and the curve fit VBM value of the bulk-like $\text{CdSe}_{0.25}\text{Te}_{0.75}$ (labeled point 1). Table 3 summarizes all the electronic features for the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surfaces described earlier.

Table 3: Salient electronic features of the low indexed $\text{Cd}_{0.25}\text{Te}_{0.75}$ surfaces. $L_{z,\text{bulk}}$ (Å) and $L_{z,\text{surf}}$ (Å) denotes the bulk electrode and the surface region length respectively. N_{atoms} represents the number of atoms within the surface region.

$\text{CdSe}_{0.25}\text{Te}_{0.75}$ Surface	$E_{\text{CdSe}_{0.25}\text{Te}_{0.75}}^g$ (eV)	E_{surf} (eV)	$L_{z,\text{bulk}}$ (Å)	$L_{z,\text{surf}}$ (Å)	N_{atoms}
(1×1) (100)	1.37	-0.25	12.10	245.48	607
$c(2 \times 2)$ (100)	1.37	-0.02	12.10	244.20	605
Unrelaxed (110)	1.36	-0.02	17.25	145.55	511
Relaxed (110)	1.36	-0.04	17.25	177.38	607
(1×1) (111)	1.39	-0.38	9.67	191.05	407
(2×2) (111)	1.37	-0.06	9.67	184.83	398

3.1. $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface

Fig. 4 shows the structural and energy band alignment features of the relaxed Cd terminated (1×1) and $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}$ surface. The $c(2 \times 2)$ surface was implemented using the (1×1) periodic unit cell in the transverse direction but required the removal of two Cd atoms from the original surface unit cell. The relaxation of (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface led to the Cd-dimer formation on the surface. Using the atomic positions of an unrelaxed (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ (see supplementary Fig. S2(a)) as a reference, it was found that the two surface Cd atoms moved towards each other by 1.866Å to form the surface Cd-dimer (Fig. 4 (c)). Similar phenomena of surface Cd-dimer formation has been reported for the (1×1) CdTe(100) surface[17].

The relaxation of $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface led to the flattening of the surface (Fig. 4 (b)). Again, using the atomic positions of an unrelaxed $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ (see supplementary Fig. S2(b)) as a reference, it was noted that surface Cd atoms shrunk by 1.374Å, while the anionic (Te/Se) layer beneath it expanded by 0.329Å in the [100] direction. Such contraction and expansion of cationic and anionic layer results in a flattened surface and has been reported in earlier CdTe(100) DFT studies[16, 17].

A Mulliken population analysis was performed on the relaxed Cd terminated (1×1) and $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface to estimate the partial atomic charges on the atoms[48]. Fig. 5 shows the partial charge distribution on the Cd, Se, and Te atoms (in terms of the electronic charge(e)) along the transverse z-direction. A positive electronic charge indicates cationic behavior, while the negative electronic charge

shows anionic behavior of the atoms. A smooth and homogeneous charge distribution was observed for both the surfaces in the bulk-like region far away from the surface as the cations and anions periodically arrange with no perturbation in the electrostatic potential. However, the lower energy configuration of atoms during relaxation causes the surface atoms to deviate from the ordered cationic/anionic arrangement. The deviation from a periodic atomic arrangement would induce a perturbation in the electrostatic potential and affect the charges on the atoms. Similar observations were made for the (1×1) and $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface. Using Fig. 5 (a), a net charge of $+1.786e$ was found to reside on the two Cd atoms forming dimers at the surface. However, for the $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface, the net surface charge added only $+0.008e$ (Fig. 5 (b)). This small amount of charge on the reconstructed surface revealed that the contraction and expansion of cationic and anionic layer observed structurally, happened to redistribute the charge. The redistributed charges with flat surface structure satisfy the Electron Counting Rule (ECR)[46] as the number of empty cation (Cd) dangling bonds become equal to the filled anionic (Te/Se) dangling bonds[17].

It is expected that the charges present on the surface influence the surface band bending. A positively charged surface is known to repel the majority hole charge carrier by bending the VBM down. Similar observations were made in the surface energy band alignment results shown in Fig. 4 (e), (f). Fig. 4 (e) shows that the (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface has a negative surface potential value of -0.25 eV (Table 3) with a high density of surface states near the valence band. A local density of state analysis (see supplementary Fig. S3) done on one of the most prominent surface state at $E = -0.61$ eV further suggests that the occurrence of such surface state is due to the Cd dimer formation in the unreconstructed $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface. However, the $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface resulted in flat bands ($E_{\text{surf}} = -0.02$ eV) with minimal density of surface states (Fig. 4 (f)). Such contrasts in the VBM bending can be attributed to the different surface charging effect observed in Mulliken population plot. A higher net surface charge of $+1.786e$ produces a larger VBM bending ($E_{\text{surf}} = -0.25$ eV) in the (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface whereas a lower surface charge of $+0.008e$ induces a smaller VBM bending ($E_{\text{surf}} = -0.02$ eV) in the $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface. In terms of charge transport, while the $c(2 \times 2)$ $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface with flat bands does not obstruct or enhance the charge carrier flow, the presence of a larger downward bend in the VBM seen in (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surface would induce a barrier for hole charge carrier transport towards the back electrode of the solar cell.

3.2. $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface

The $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface is non-polar since the (110) plane contains equal numbers of cations and anions. As discussed earlier, the (110) plane has the lowest cleavage energy as it inherently satisfies the ECR. Previous literature studies for III-V(110) surface have reported about 28° - 32° atomic chain tilt on the top (110) surface layer[46]. Similar atomic chain tilt features with a tilt angle(ω) of 30° have been observed experimentally for the $\text{CdTe}(110)$ surface[49]. Another *Ab-initio* study using DFT has reported 30.2° and 27.1° tilt angle for the respective $\text{CdTe}(110)$ and $\text{CdSe}(110)$ surfaces[15].

Fig. 6 shows the structural and electronic features of an unrelaxed and relaxed $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface. The structural comparison between the unrelaxed and relaxed $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface showed the classic atomic chain tilt observed in other III-V(110) and II-VI(110) surfaces. It can be seen that the surface relaxes with surface anions (Te/Se) moving out (vertical buckling($\Delta_{\perp,1}$)) of the (110) plane and surface cations moving inwards. Previous studies with binary alloys have reported only a single vertical buckling parameter for the cation and anion[15, 46]. However, with the ternary $\text{CdSe}_{0.25}\text{Te}_{0.75}$ alloy, it was observed that the vertical buckling of Cd atom (labeled in Fig. 6 (b) subfigure) was dependent on the anion atom (Te or Se) lying directly beneath it. Similarly, the vertical buckling of the Te and Se anions differed and has been summarized in Table 4. The difference in the electronegativity of the Se and Te atoms causes variation in vertical buckling values for anions and is consequently reflected in the corresponding Cd atom attached to either of the anions. *Watari et. al.* made similar observations where the more electronegative Se anion has less vertical buckling than the Te anion[15].

Fig. 6 (b) and (d) shows the *pyramidal angle* α at the anion, the *in-plane angle* β and the *planar angle* γ at the cation. Due to the difference in relaxation of the Se and Te anion, each of the above listed angles measured different values. The *pyramidal* and *in-plane angles* measured for Se anions were labeled as α_1

Table 4: Vertical buckling values of the surface Cd, Se and Te atom. The $\leftarrow$ and $\rightarrow$ symbols indicate respective atoms moving inward and outward of the (110) surface plane.

Atoms	Cd ₁	Cd ₂	Se	Te
$\Delta_{\perp,1}$	$\leftarrow 0.528 \text{ \AA}$	$\leftarrow 0.536 \text{ \AA}$	$\rightarrow 0.135 \text{ \AA}$	$\rightarrow 0.323 \text{ \AA}$

and β_1 respectively, while for the Te anions they were designated as α_2 and β_2 . Similarly, the *planar angles* at the cation were labeled as γ_1 and γ_2 for the Te-Cd-Se and Se-Cd-Te measurements respectively (shown in Fig. 6 (b) subfigure). In addition to the difference between the above angles, the *tilt angle* ω_1 computed for the plane containing Cd₁ and Se atom differed from the *tilt angle* ω_2 calculated for the plane containing Cd₂ and Te atom. All the angles with their respective values obtained in this calculation are summarized in Table 5.

The trend of *pyramidal angle* α being closer to 90° and decreasing from 92.5° for Se to 85.5° for Te atom is in agreement with the binary CdTe and CdSe alloy. The *planar angle* γ at the cation is close to 120° as the surface cation atoms prefer sp^2 -like hybridization. The *in-plane angle* β is lower than γ and is closer to the tetrahedral bond angle of 109.47° as the anions prefer sp^3 -like hybridisation with their three cation neighbors. The *tilt angle* ω also lies close to the expected 30° mark but its exact value needs to be verified experimentally. In general, all the angles calculated for relaxed CdSe_{0.25}Te_{0.75}(110) surface in this study are in qualitative agreement with the published literature values[15].

Table 5: Calculated tilt angle and bond angle values for anions and cations.

Angles	α_1	α_2	β_1	β_2	γ_1	γ_2	ω_1	ω_2
Values	92.5°	85.5°	114.4°	116.6°	118.5°	126.5°	33.73°	31.33°

The net charge on each surface estimated using the Mulliken population analysis for the unrelaxed and relaxed CdSe_{0.25}Te_{0.75}(110) surface was found to be ~ 0 . This net surface zero charge implies a neutral surface and was expected as the (110) maintains stoichiometry. However, a decrease in the positive cationic and negative anionic electronic charge was observed for the relaxed CdSe_{0.25}Te_{0.75}(110) surface when compared to the unrelaxed case. Such changes in the partial charges before and after surface relaxation suggest a charge transfer from the anionic Se/Te to cationic Cd atoms. A net 0.158e charge transfer from the anions (Se and Te combined) to the surface Cd cations was determined using the data points from Fig. 7 (a) and (b). It is hypothesized that this charge transfer between the cations and anions occurs due to the tilting of the (110) surface. A similar charge transfer of 0.75e from the cation to anion has been reported earlier due to the tilting of III-V(110) binary alloy surface[46].

The energy band alignment diagrams shown in Fig. 6 (e) and (f) for the respective unrelaxed and relaxed CdSe_{0.25}Te_{0.75}(110) surfaces results in flat bands. The cleavage along the (110) plane creates a clean electronic surface as no surface states are observed in the energy band alignment diagrams. The flat bands were anticipated for the non-polar (110) surface as no surface charging effect was observed in the partial atomic charge distribution. As discussed previously, the presence of such flat bands would neither enhances nor obstruct the charge carrier transport towards the back electrode of the solar cell device.

3.3. CdSe_{0.25}Te_{0.75}(111) surface

Regarding Cd terminated CdSe_{0.25}Te_{0.75}(111) surface, Fig. 8 shows the structural and electronic features of the (1×1) unreconstructed and (2×2) reconstructed surface. The relaxed (1×1) CdSe_{0.25}Te_{0.75}(111) surface in Fig. 8 (a) clearly demonstrates that the (2×2) reconstructed surface would be an energetically favorable facet. This is verified by the fact that after the relaxation of the (1×1) unreconstructed

surface, a surface Cd atom is displaced in the $[111]$ direction by $1.549 \text{ \AA}$ from its original position in the unrelaxed surface. It was also noted that the atomic rearrangement of the surface atoms due to the relaxation of $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ surface generated a flat surface. Using the positions of the unrelaxed (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ (see supplementary Fig. S3(a)) surface as a reference, the Cd terminating layer contracted by $0.926 \text{ \AA}$ and the Te and Se atoms beneath it expands by $0.107 \text{ \AA}$ and $0.123 \text{ \AA}$ respectively. A Similar surface flattening was observed in the relaxed (2×2) $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ surface. Again, using the unrelaxed (2×2) (see supplementary Fig. S3(b)) case as a reference, it was found that surface Cd terminating layer shrunk by $0.808 \text{ \AA}$, while the Te and Se atoms beneath it expands by $0.169 \text{ \AA}$ and $0.099 \text{ \AA}$ respectively. Such flattening of the surface observed for the (2×2) $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ model was in agreement with the other calculations done for (2×2) $\text{CdTe}(111)$ and III-V(111) surface[17, 46].

The partial atomic charge distribution plotted using Mulliken population analysis, showed surface charging effect in (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ surface. Using Fig. 9 (a), it was estimated that the displaced Cd atom in (1×1) surface had an extra $+0.289e$ charge, while the reconstructed (2×2) surface was found charge neutral (Fig. 9 (b)). It was thus inferred that the charge neutrality in reconstructed (2×2) surface was due to the missing surface Cd atom. The flattening of surface also played a role in achieving a neutral surface. Previous DFT studies for $\text{CdTe}(111)$ had attributed flattening of (2×2) reconstructed surface as a means of satisfying ECR[17]. This was again validated for (2×2) $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ surface with the above reasoning. As discussed earlier for (100) surface, the effects of surface charging on the energy band alignment was observed in (1×1) (111) surface. The positive charge at the surface bent the VBM down(Fig. 8 (e)). High density of the surface states also resulted from the displaced surface Cd atom showing that the (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ surface is not clean. The LDOS calculation (see supplementary Fig.S4) at $E = -0.35 \text{ eV}$ for one of the prominent surface state further verifies the fact that the displaced Cd atom contributes to the high density of surface state in the (1×1) $\text{CdSe}_{0.25}\text{Te}_{0.75}(111)$ surface. However, due to surface charge neutrality no band bending was seen in the reconstructed (2×2) surface(Fig. 8 (f)). The presence of a hole barrier in (1×1) surface would impede the majority hole carrier (for p-doped CdSeTe absorber) transport in unreconstructed surface in comparison to the reconstructed (2×2) surface.

4. CdTe vs $\text{CdSe}_{0.25}\text{Te}_{0.75}$: Surface energy band alignment comparison

Fig. 10 (a) and (b) compares the surface energy band alignment of the polar (100) and (111) facets of CdTe and $\text{CdSe}_{0.25}\text{Te}_{0.75}$ alloy. This comparison was done to explain one of the potential reasons (but not limited to) for lower performance of CdSeTe-only devices in contrast to CdTe-only devices. Fig. ?? (c) shows the current density vs voltage measurement comparison for one of the high performing CdSeTe-only and CdTe-only devices. It was noted that CdSeTe-only device was 10.27% efficient whereas an efficiency of about 15.4% was recorded with the CdTe-only device. Table 6 summarizes the measurements performed on both the device.

Table 6: J-V measurement comparison of the performance of CdSeTe-only and CdTe-only solar cells.

Absorber layer	J_{SC} (mA/cm ²)	V_{OC} (mV)	%FF	% η
CdSeTe	26.4	662	58.7	10.27
CdTe	25.7	817	72.7	15.24

While the CdSeTe-only device showed a relatively higher short circuit current (J_{SC}) value than CdTe-only device(CdSeTe being a lower bandgap material than CdTe), other parameters such as open circuit voltage (V_{OC}) and the Fill Factor (%FF) were notably smaller. The lower performance of CdSeTe-only absorber based solar cell device indicates a higher recombination and an inferior charge transport when compared to CdTe-only absorber based device. The comparison of the $\text{CdSe}_{0.25}\text{Te}_{0.75}$ and CdTe surface energy band alignment diagrams calculated using DFT gave further insights into the features affecting

the charge transport in CdTe and CdSe_{0.25}Te_{0.75} layers. *Nicholson et. al.* showed a cusp feature in the CdTe surface calculations and credited this feature to be beneficial for hole charge transport towards the back electrode of the device[17]. Previous theoretical and experimental studies on CdTe/Te interface have also shown the presence of a similar cusp feature as seen in the DFT CdTe surface calculations[18, 50]. While a cusp feature in the valence band has been observed in CdTe surface and interface calculations, no such feature was observed in the DFT study of CdSe_{0.25}Te_{0.75} surfaces. The absence of such feature from the CdSe_{0.25}Te_{0.75} surface energy band alignment diagram would be reflected in the hole charge carrier transport leading to a lower device performance when compared to CdTe-only absorber based PV devices. Further, lower performance of CdSeTe-only devices could also be due to presence of high defect density at MZO/CdSeTe and CdSeTe/Te interfaces in addition to the absence of key cusp feature in CdSeTe surfaces. The DFT study probing the energy band alignment diagrams of the interface is in progress and the results will be reported subsequently. As pointed before, Se tends to exhibit a random distribution in the CdSe_xTe_{1-x} alloy, however the random distribution of Se using SQS presents a computational challenge (due to high number of atoms) with the current one-probe model to study the CdSeTe surface. Nonetheless, at least from a first-order perspective the comparison of electronic features in CdSeTe surface (Se in fixed regular lattice position) with CdTe provides useful insights into the difference in the electronic structure observed in the ternary CdSeTe alloy absorber.

5. Conclusion

In summary, DFT + SGF approach was applied to three principle low indexed CdSe_{0.25}Te_{0.75} surface facets. The non-polar (110) surface facet due to a charge neutral surface generated a flat CBM and VBM. The polar (100) and (111) surfaces were studied with the Cd-termination layer. In general, the (1 × 1) CdSe_{0.25}Te_{0.75}(100) and (111) unreconstructed surfaces showed the downward bending in the VBM. The resulting downward bend in the VBM was due to the positively charged surface as observed in the Mulliken population analysis. However, the c(2 × 2) and (2 × 2) reconstructed CdSe_{0.25}Te_{0.75}(100) and (111) surfaces result in the cleaner energy band diagrams with minimal surface states. The comparison between unreconstructed and reconstructed surface depicts the importance of different surface defects in their respective plane orientations.

Further comparison of the CdTe surface electronic features with those of CdSe_{0.25}Te_{0.75} revealed the possible reason for lower performance of CdSeTe-only devices observed experimentally. Earlier studies have shown the prominence of the additional cusp feature observed in the CdTe surface and CdTe/Te interface for hole carrier transport in CdTe PV device. The absence of the cusp feature from CdSe_{0.25}Te_{0.25} surface may lead to a depreciated device performance. These results also suggest the importance of including the CdTe layer at the back of CdSeTe absorber for effective charge transport.

Overall, the atomistic modeling perspective of CdSeTe surfaces provides insight into spatial distribution of the electronic features. A good understanding of the CdSeTe surfaces would lead to a better comprehension of the different CdSeTe interfaces and will help in further improving the device performance of II-VI absorber based solar cells.

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7. Supplementary Information

- Filename: Supplementary data and figures CdSeTe surface

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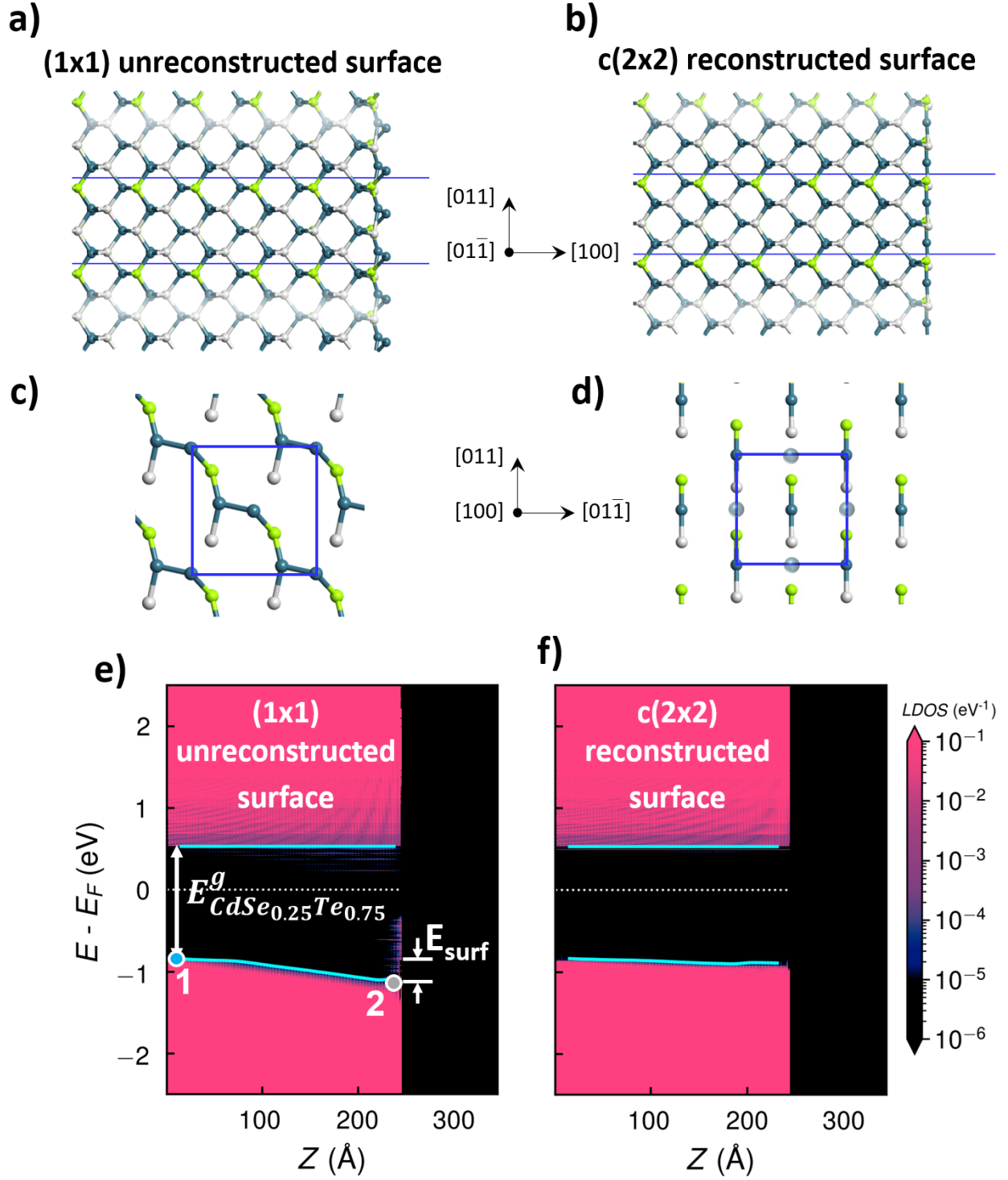


Figure 4: Side view and the top view of the respective relaxed atomic configurations of (a,c) the (1×1) unreconstructed and (b,d) the $c(2 \times 2)$ reconstructed $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surfaces. The top view shows the last two atomic layers of the surface for clarity. The side view is shown along the transport direction. The blue translucent spheres in (d) represent the missing Cd atom in $c(2 \times 2)$ reconstructed surface. (e) and (f) shows the energy band alignment diagram of the respective relaxed atomic configurations of the (1×1) unreconstructed and the $c(2 \times 2)$ reconstructed $\text{CdSe}_{0.25}\text{Te}_{0.75}(100)$ surfaces. The dotted line indicates the fermi energy level and the blue curves are the trace of the macroscopic average fits of the VBM and CBM.

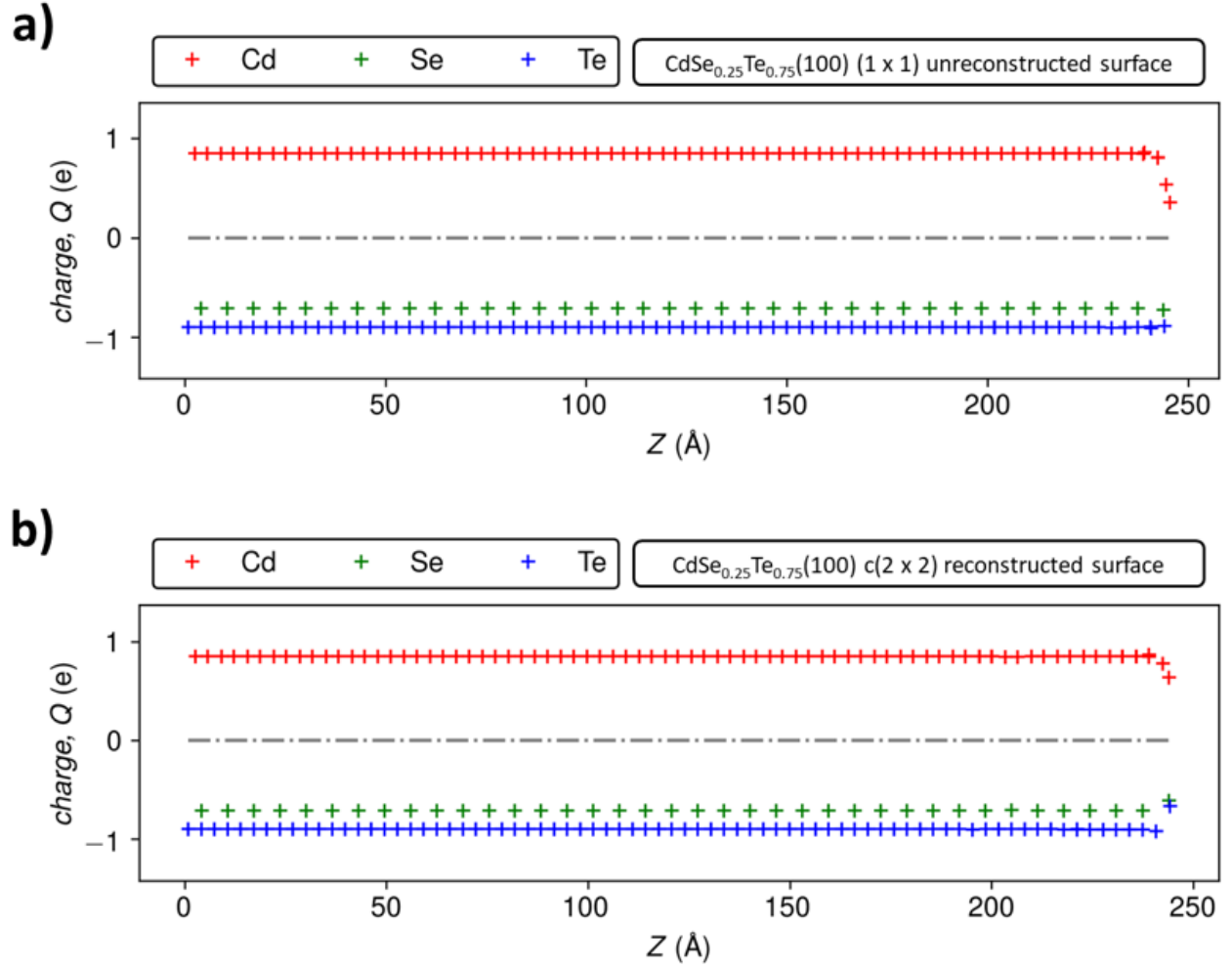


Figure 5: Mulliken population analysis showing the atomic charge distribution for (a) (1 × 1) CdSe_{0.25}Te_{0.75}(100) surface and (b) c(2 × 2) CdSe_{0.25}Te_{0.75}(100) surface.

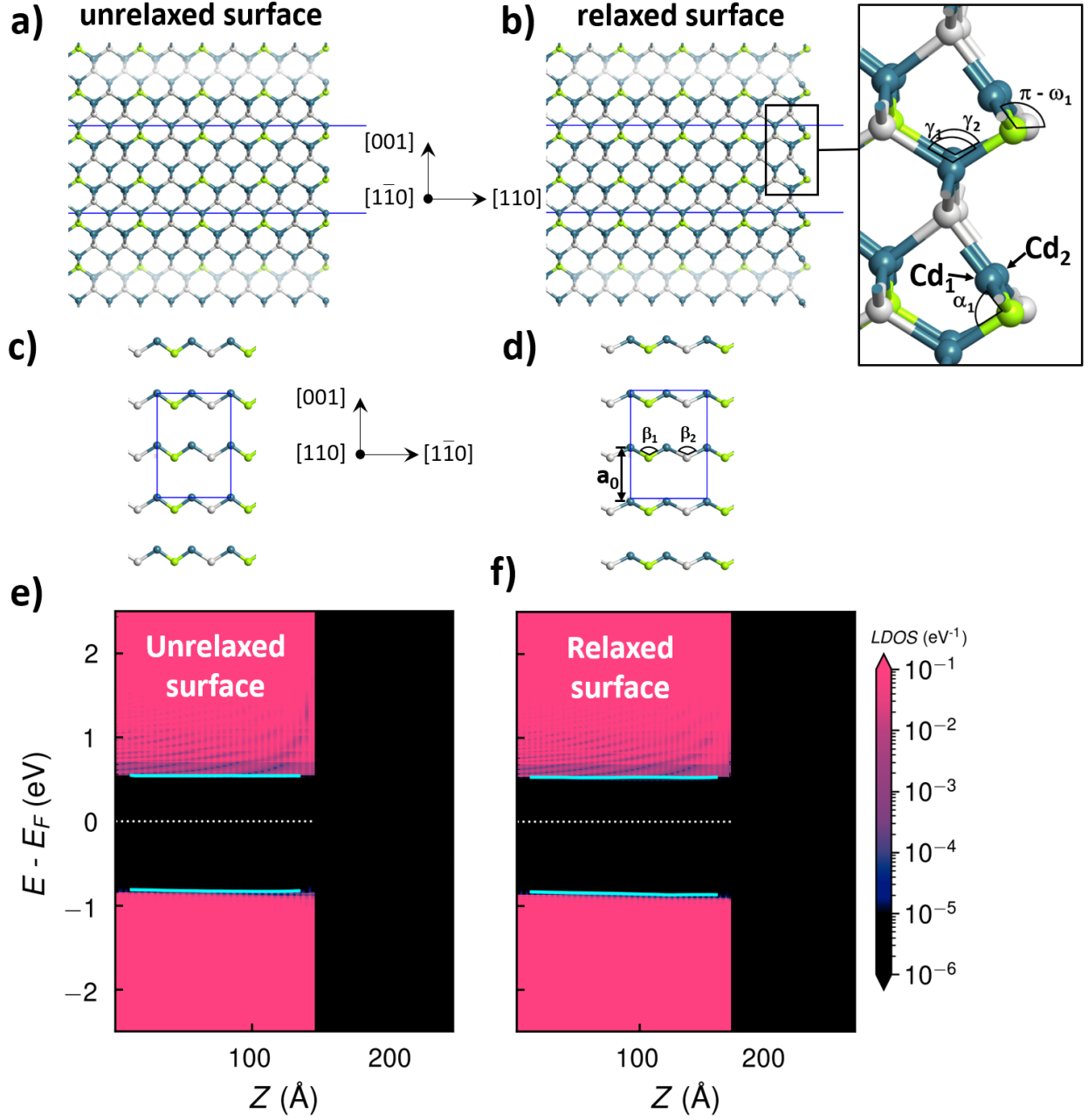


Figure 6: Side view and the top view of the respective atomic configurations of (a,c) the unrelaxed and (b,d) the relaxed $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface. The top view shows the last two atomic layers of the surface for clarity. The side view is shown along the transport direction. The subfigure in (b) shows the tilt angle and the bond angles measured for cations and anions. In (d), parameter $a_0 = 6.48 \text{ \AA}$ measures the lattice constant of the bulk $\text{CdSe}_{0.25}\text{Te}_{0.75}$. (e) and (f) shows the energy band alignment diagram of the respective atomic configurations of the unrelaxed and the relaxed $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface.

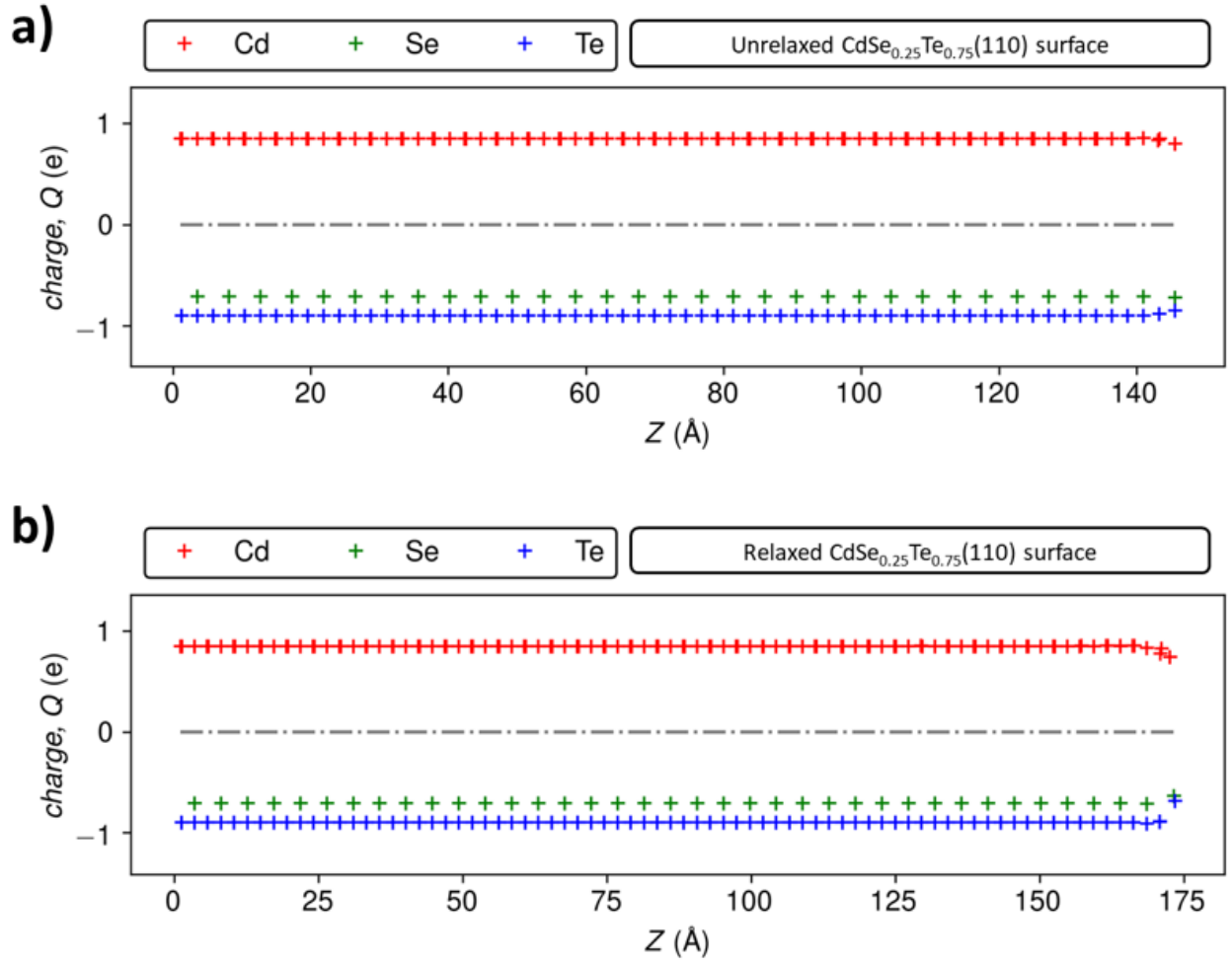


Figure 7: Mulliken population analysis showing the atomic charge distribution for (a) unrelaxed $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface and (b) relaxed $\text{CdSe}_{0.25}\text{Te}_{0.75}(110)$ surface.

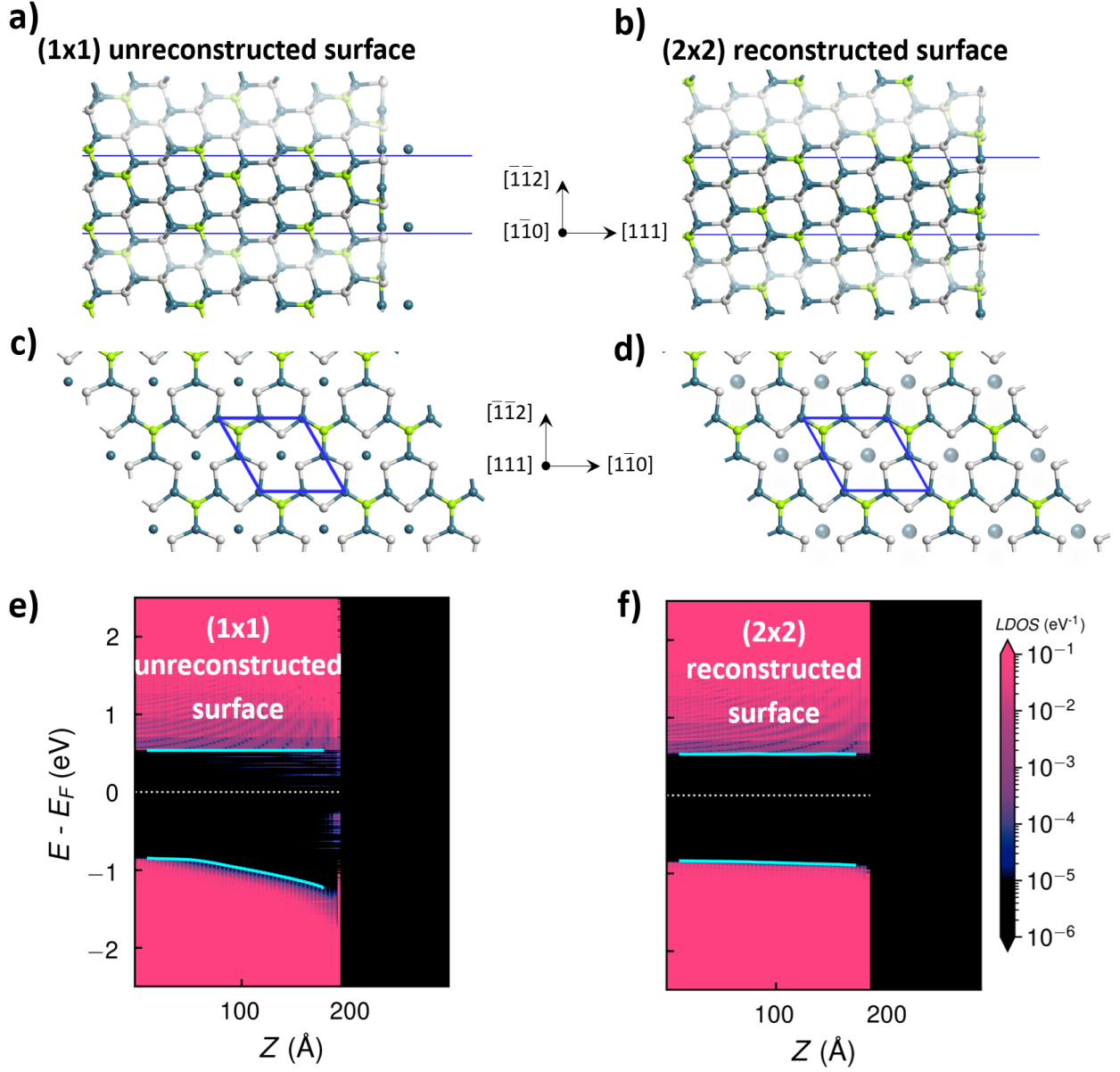


Figure 8: Side view and the top view of the respective relaxed atomic configurations of (a,c) the (1×1) unreconstructed and (b,d) the (2×2) reconstructed CdSe_{0.25}Te_{0.75}(111) surfaces. The top view shows the last two atomic layers of the surface for clarity. The side view is shown along the transport direction. The blue translucent spheres in (d) represent the missing Cd atom in (2×2) reconstructed surface. (e) and (f) shows the energy band alignment diagram of the respective relaxed atomic configurations of the (1×1) unreconstructed and the (2×2) reconstructed CdSe_{0.25}Te_{0.75}(111) surfaces.

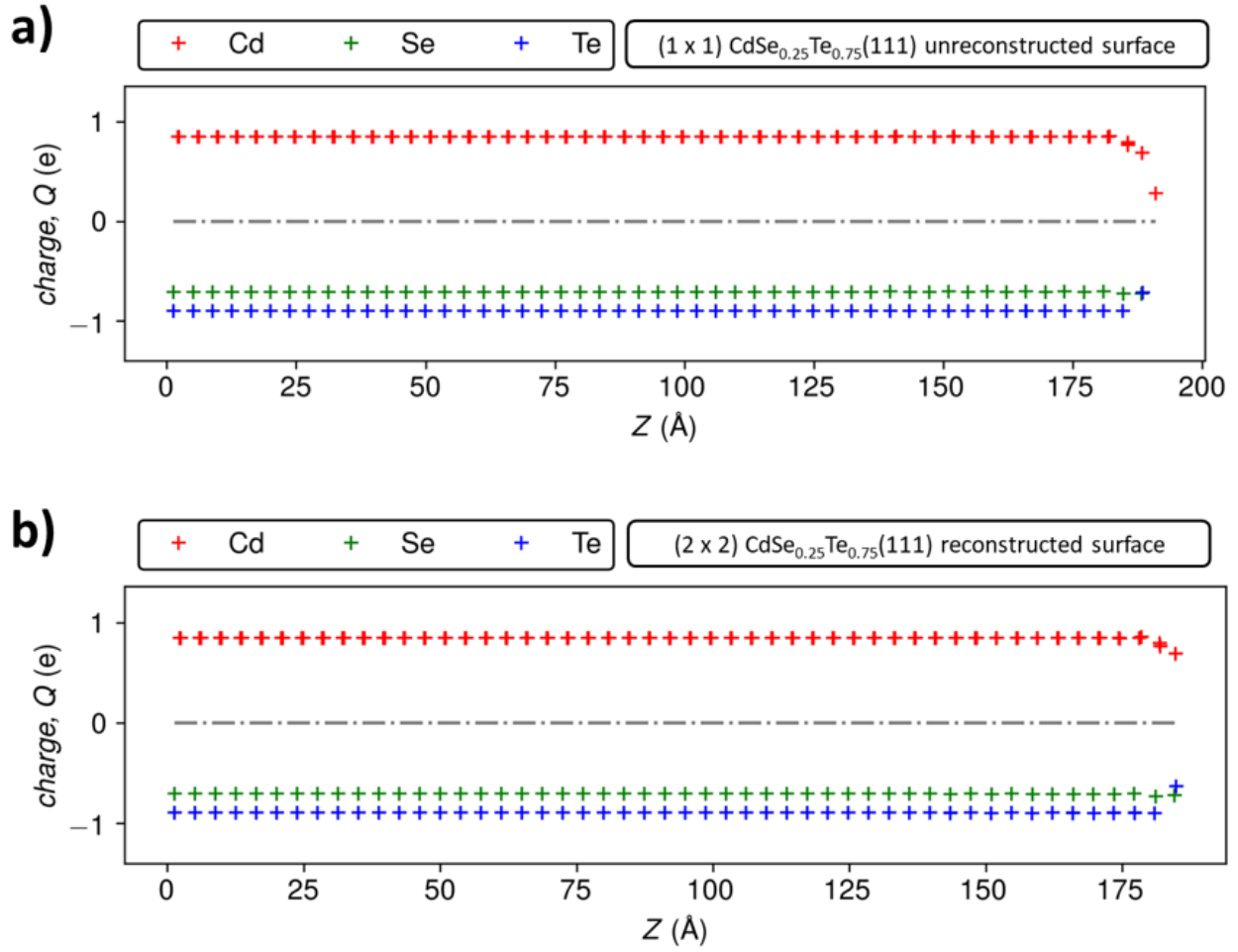


Figure 9: Mulliken population analysis showing the atomic charge distribution for (a) (1 × 1) CdSe_{0.25}Te_{0.75}(111) surface and (b) (2 × 2) CdSe_{0.25}Te_{0.75}(111) surface.

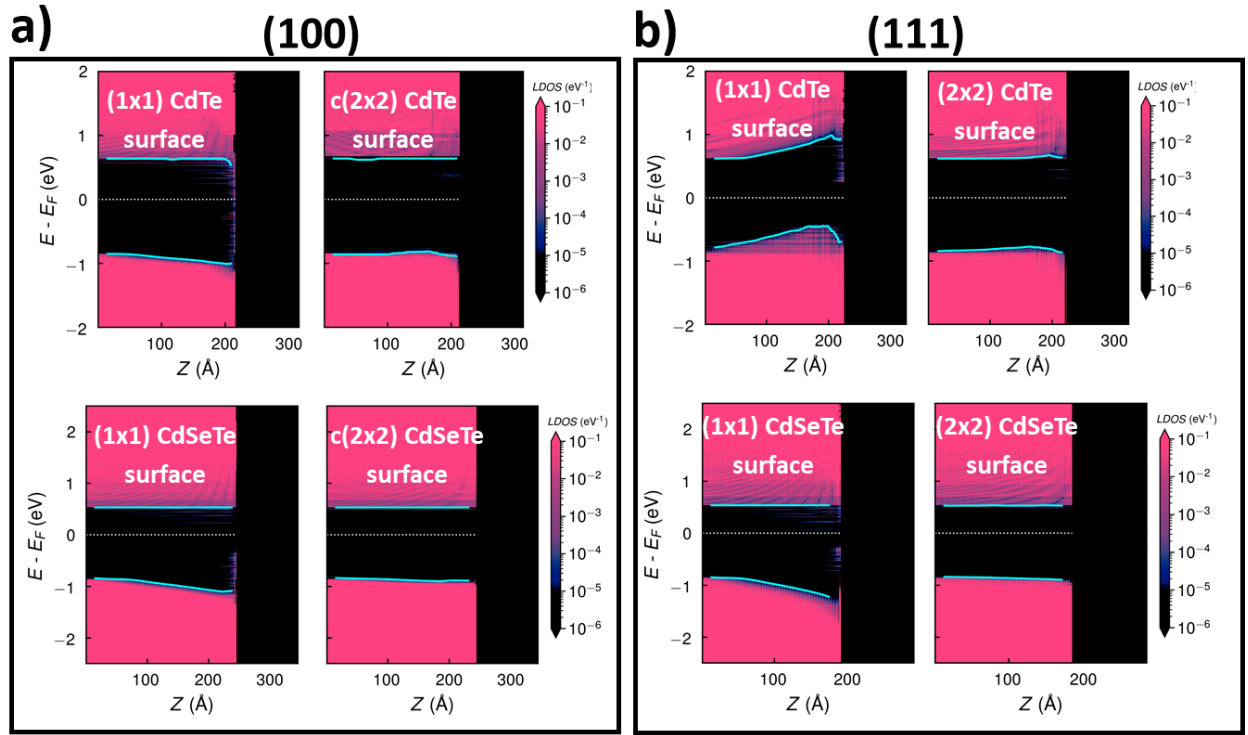


Figure 10: Energy band alignment comparison of unreconstructed and reconstructed CdTe and CdSe_{0.25}Te_{0.75} (a) (100), (b) (111) surface facets. The CdTe surface energy band alignment results were adapted from *Nicholson et. al.*[17], with permission.

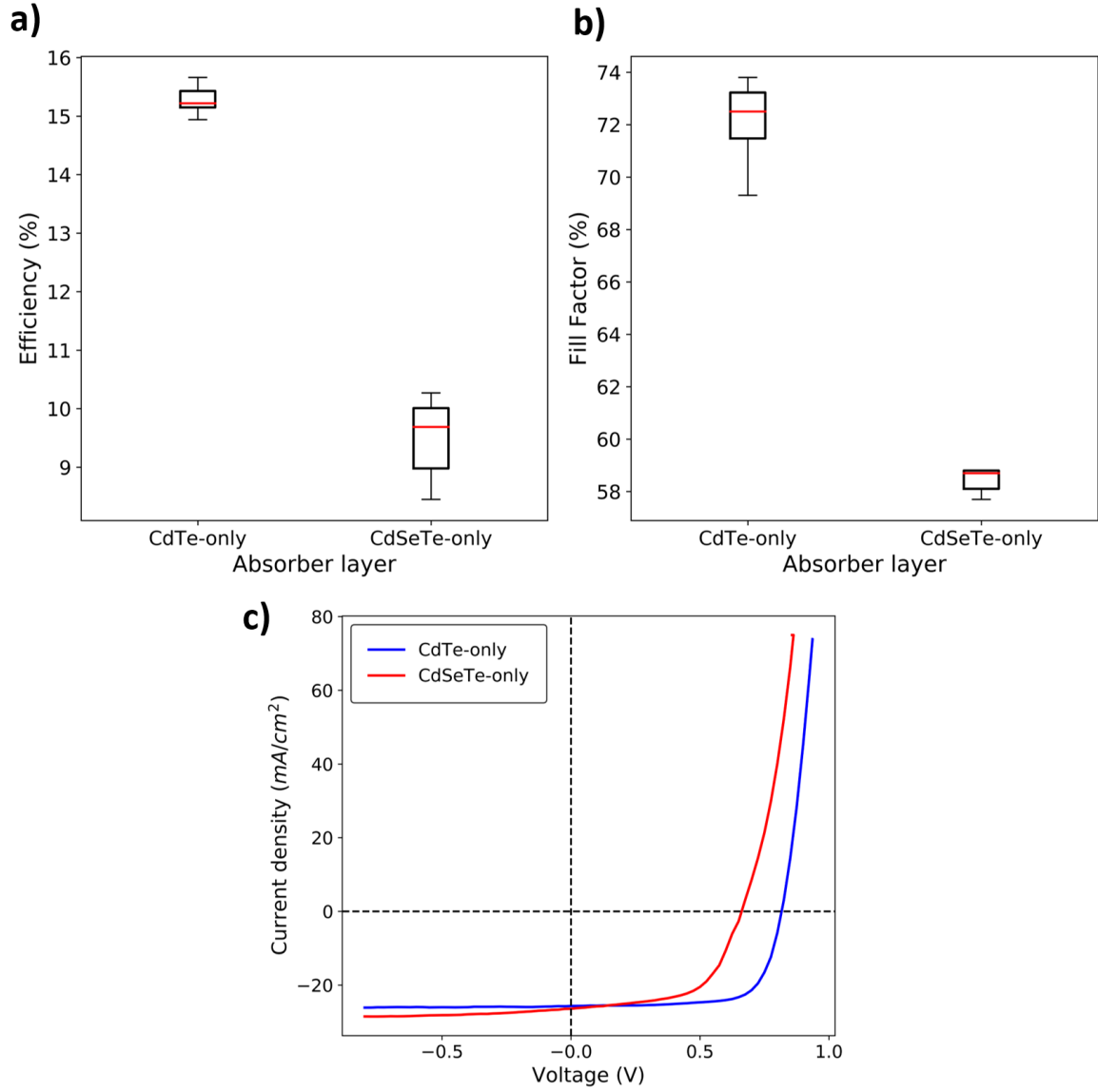
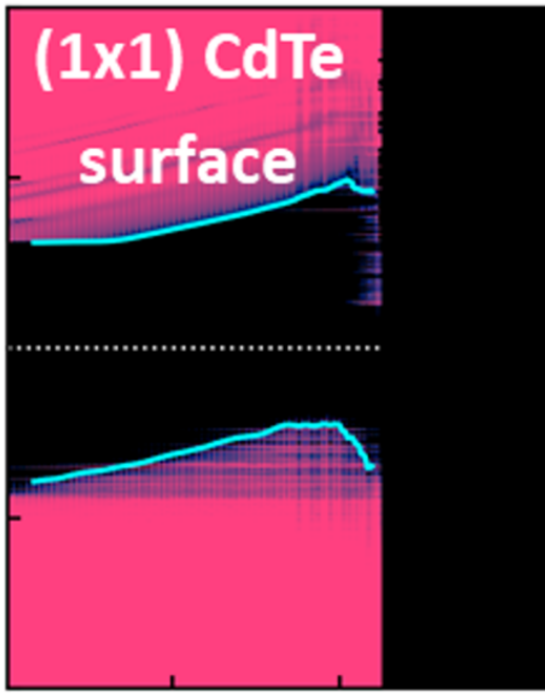
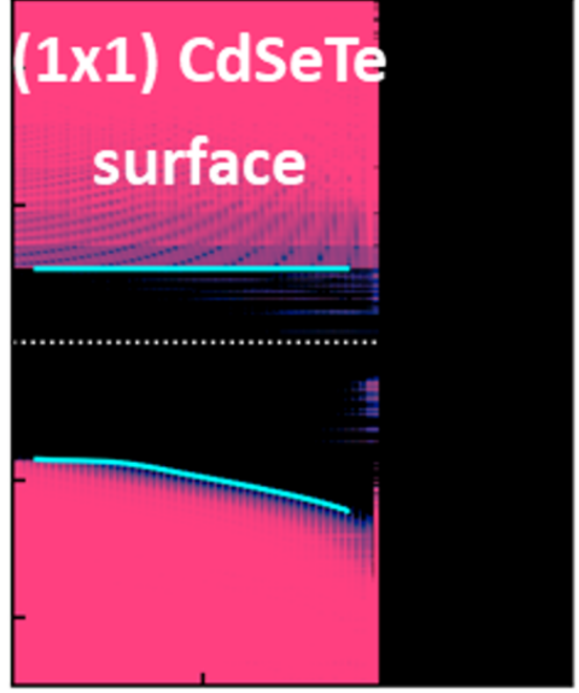


Figure 11: Box plot comparing the (a) % Efficiency and (b) % Fill Factor between CdTe-only and CdSeTe-only absorber based solar cells. (c) compares the device performance between CdTe-only and CdSeTe-only solar cell. The CdTe-only absorber based solar cells produced always produced higher efficiency device than the CdSeTe-only absorber device.

Surface Energy Band alignment



100 200 300
Z (Å)



100 200
Z (Å)



Semiconductor PV device performance

