Rapid Recombination by Cadmium Vacancies in CdTe

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Cadmium telluride (CdTe) is a well-studied thin-film photovoltaic (PV) absorber, being one of few solar technologies to achieve commercial viability.1 Its ideal 1.5 eV electronic band gap and high absorption coefficient have allowed it to reach record light-to-electricity conversion efficiencies of 22.1%.2,3 Given that device architectures and large-scale manufacturing procedures have been highly optimized for this technology—a result of several decades of intensive research3,4—further reductions in cost will be heavily dependent on improvements in photoconversion efficiency.1,2,5,6

Indeed, under the idealized detailed balance model, CdTe has an upper limit of 32% single-junction PV efficiency (based on its electronic bandgap),7 indicating that there is still room for improvement.6,8

Despite over 70 years of experimental and theoretical research,1,2,12−19 the defect chemistry of CdTe is still not well understood. The unambiguous identification of the atomistic origins of many experimentally observed spectroscopic signatures remains elusive. Only through clear understanding of defect behavior can strategies be devised to avoid and/or mitigate their deleterious effects on device performance.9,10

At present, market-leading CdTe solar cells employ a Te-rich p-type CdTe absorber layer, favoring the formation of Cd vacancies. Indeed, undoped CdTe grown from the melt is typically found to exhibit native p-type behavior,11,14 which has often been attributed to the presence of vacancies in the Cd sub-lattice (and/or Te-on-Cd antisites).18 However, the exact origin of this low intrinsic p-type conductivity is still not well understood, with difficulties in definitive measurements14−16,24 and discrepancies between models and observations.2,5,25−28

While there is consensus that the cadmium vacancy (V_{Cd}) is an important acceptor species in CdTe, strong debate has endured regarding its structural and electronic behavior.2,14,16,26−32

The ability of modern theoretical approaches to accurately describe defect behavior is well established.20,33,35 The use of a sufficiently accurate Hamiltonian is essential for reliable predictions. For CdTe, using a screened hybrid Density Functional Theory (DFT) functional with spin−orbit coupling (HSE+SOC), we find that the room-temperature experimental bandgap of 1.5 eV is reproduced at a Hartree−Fock exchange fraction α_{inh} = 34.5%, a value which also reproduces the experimental lattice constant to within 1% (see Supporting Information). For consistency, this model was employed in all structural optimizations and electronic calculations.

Cadmium Vacancy: Equilibrium Structures. The first step in any theoretical investigation of solid-state defects is the determination of their equilibrium structures. CdTe crystallizes in the zinc-blende structure (space group F\text{4}3\text{m}), thus exhibiting tetrahedral (T_d) symmetry at both the Cd and Te sites. The relaxed geometric configurations upon creation of a cadmium vacancy in the neutral (V_{Cd}^0), single-negative (V_{Cd}^-), and double-negative (V_{Cd}^{2-}) charge states are shown in Figure 1. Only the double-negative defect retains the original tetrahedral point-group site symmetry, with a contraction of the
neighboring Te atoms from the original bond distance of 2.83 Å to 2.61 Å from the vacancy center-of-mass.

The defect site distortions can be rationalized through consideration of the local bonding behavior in a molecular orbital model.36,37 Removal of a Cd atom (and its two valence electrons) to create a vacancy results in a fully occupied A1 electron level and a two-thirds occupied T2 level at the Fermi level, arising from the tetrahedral coordination of Te sp^3-hybrid orbitals. In the double-negative case (VCd^2^−), the T2 level becomes fully occupied, and thus tetrahedral point symmetry is maintained (Figure 1a), with the Te atoms moving closer to the vacancy site to allow for greater hybridization between dangling bonds.

For the singly charged vacancy, the 5/6 partial occupancy of the T2 level is unstable, undergoing a trigonal Jahn–Teller distortion that substantially elongates one of the Te neighbor distances (Figure 1b). In this C3v-symmetry vacancy coordination, a positive hole is strongly localized on the Te atom furthest from the vacancy site, as depicted in Figure 2a, resulting in a paramagnetic defect species. This C3v polaronic structure of VCd^1^− was experimentally identified in the 1990s, using electron paramagnetic resonance (EPR),14,16 but was only reproduced for the first time in a 2015 theoretical study by Shepichenko et al.38 using the HSE06 functional. The primary reason why previous ab initio works2,25,28,39−42 have failed to identify this polaronic ground-state structure for VCd^1^− is the spurious electron self-interaction and consequent over-delocalization inherent in standard (semi)local DFT functionals.20,43−45

In the neutral case, we find that the Cd vacancy undergoes strong local relaxation to a C2v structural motif, whereby two Te atoms move significantly closer both to the vacancy site and to each other (2.75 Å separation from an initial 4.63 Å) (Figure 1c). This yields a Te dimer arrangement with occupied sp^3-σ-bonding electronic levels deep in the valence band and unoccupied antibonding states in the conduction band (Figure 2b). Notably, this Te dimerization resembles that observed at low-energy surfaces and grain boundaries in CdTe and has been suggested as a source of fast recombination at these locations. Similar metal–metal dimer reconstructions have been noted for neutral anion vacancies in the II–VI semiconductors ZnSe and ZnS,48 occurring here for the cation vacancy in CdTe due to the metalloid character of the Te anion.

This atomic reconstruction reduces the vacancy formation energy by 0.52 eV, relative to the tetrahedral solution that has been widely reported28,39−42,49−51 (Figures 3 and 4). As with

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been identified\textsuperscript{18} The tetrahedral and bipolaron \textsuperscript{(Figure 2c)} configurations are in fact local minima on the defect potential energy surface (PES), as shown in Figures 3, 4, and S7.

The electronic behavior of the Cd vacancy is dramatically affected by Te dimerization, as the singly charged state V\textsubscript{Cd}\textsuperscript{+} is consequently predicted to be thermodynamically unfavorable across all Fermi energies (Figure 4). Accordingly, the vacancy is predicted to act as a so-called negative-U center,\textsuperscript{52,53} with a single double-acceptor level at 0.35 eV above the valence band maximum (VBM). This is in excellent agreement with experimental reports of a single \textit{thermal} ionization level in the bandgap at 0.3–0.4 eV above the VBM (Table S1).\textsuperscript{29,31,32,54–58} Moreover, negative-U behavior helps to explain apparent discrepancies between experimental reports of Cd vacancy trap levels, as different techniques can measure either the single-charge (2\textsuperscript{−} \rightarrow 1\textsuperscript{−} and 1\textsuperscript{−} \rightarrow 0) or double-charge transitions (2\textsuperscript{−} \rightarrow 0).\textsuperscript{59} The reasons previous theoretical works have not identified this behavior are twofold: namely, incomplete mapping of the defect potential energy surface (overlooking Te–Te dimerization in V\textsubscript{Cd}\textsuperscript{0}) and qualitative errors in lower levels of electronic structure theory (destabilizing localized solutions; viz. the V\textsubscript{Cd}\textsuperscript{0} small-polaron); see Supporting Information, Section S6, for further discussion.

\textbf{Optical Response.} The paramagnetic nature of the single negative charge vacancy V\textsubscript{Cd}\textsuperscript{−} (due to the presence of an odd number of electrons) lends itself to experimental identification through electron spin resonance (ESR/EPR) spectroscopy. In 1993, Emanuelsson et al.\textsuperscript{14} used photo-ESR to identify the C\textsubscript{3v} coordination of V\textsubscript{Cd}\textsuperscript{−} with a localized hole on a Te neighbor as predicted here (Figure 2a). After thermal annealing at 750 °C, they obtained a p-type CdTe film with a carrier concentration \(p = 1.2 \times 10^{17} \text{ cm}^{-3}\), in excellent agreement with our predicted maximum hole concentration of \(p = 4.2 \times 10^{17} \text{ cm}^{-3}\) at this temperature (based on calculated intrinsic defect formation energies). While V\textsubscript{Cd}\textsuperscript{−} is never the lowest energy configuration at equilibrium, we find that Cd vacancies do in fact adopt this charge state under high-temperature \(p\)-type growth conditions, as a consequence of energy minimization within the constraint of charge neutrality (to counteract the large hole concentration).

Emanuelsson et al.\textsuperscript{14} interpreted a decrease in the V\textsubscript{Cd}\textsuperscript{−} ESR intensity upon irradiation with photons of energy \(h\nu > 0.47 \text{ eV}\) as the optical excitation of an electron from the valence band to the \((-2-) V\textsubscript{Cd} level, to produce V\textsubscript{Cd} + h\nu\textsubscript{VBM}. Using the defect structures obtained in our investigations, we calculate the peak energy of 0.58 eV, with vibronic coupling estimated to give a Gaussian line shape with a fwhm of 0.12 eV, yielding good agreement with experiment (Figure 5).

\textbf{Trap-Mediated Recombination.} To determine the non-radiative recombination activity, electron and hole capture coefficients were calculated for each charge state of the defect. This approach, building on the developments of Alkauskas et al.,\textsuperscript{60} uses the CarrierCapture.jl package,\textsuperscript{61} and full details of the calculation procedure are provided in the Supporting Information, Section S8. The PES of the defect is mapped along the structural path (configuration coordinate) \(Q\) between the equilibrium geometries for a given charge transition, from which nuclear wave function overlaps can be determined via the 1D Schrödinger equation.\textsuperscript{62,63} Electron–phonon coupling is then calculated under static coupling perturbation theory which, in combination with phonon overlaps and scaling factors for charge interaction effects, yields the carrier capture coefficients \(C_{\text{h/e}}^{\text{Q}}\).

The energy surfaces for all in-gap V\textsubscript{Cd} carrier traps are shown in Figure 6 and the resulting capture coefficients tabulated in the Supporting Information, Section S8. As expected for an acceptor defect with a trap level near the VBM (Figure 4), hole capture is fast while electron capture is slow for the \((-2-)\) transition, with small and large capture barriers, respectively. For the \((-1-) \rightarrow \text{V}_{\text{Cd},\text{Te Dimer}}\) transitions, however, the behavior is drastically different to that predicted by a simple quantum defect model.\textsuperscript{63} First, hole capture is more rapid than expected, due to the ability of V\textsubscript{Cd} to transition to the metastable V\textsubscript{Cd,Bipolaron} configuration, before relaxing to the V\textsubscript{Cd,Te Dimer} ground state. Second, despite the \((-1-) \rightarrow \text{V}_{\text{Cd},\text{Te Dimer}}\) transition, we in fact find a giant electron capture coefficient. This unusual behavior is a direct result of the anharmonicity of the PESs at this trap center, accompanied by large electron–phonon coupling, through Te dimer formation.
These findings provide additional evidence to support Te dimerization at surfaces and grain boundaries in CdTe as a cause of high recombination velocities at these locations. Consequently, the \((-0)_{\text{CdTe}}^{0}\) charge transition is predicted to facilitate rapid electron–hole recombination, proceeding via the \(\{\text{V}^{0}_{\text{Cd}}, \text{Te Dimer} + \text{e}^{-}_{\text{CBM}} + h^{+}_{\text{VBM}}\} \rightarrow \{\text{V}^{0}_{\text{Cd, Bipolaron}} + \text{e}^{-}_{\text{CBM}}\} \rightarrow \{\text{V}^{0}_{\text{Cd, Te Dimer}} + \text{e}^{-}_{\text{CBM}}\} \rightarrow \{\text{V}^{0}_{\text{Cd}}\} \) cycle shown in Figure 6b. Notably, the large capture coefficients for the rapid (green) processes are comparable to the most deleterious extrinsic defects in silicon and the kesterite photovoltaic family. This classifies \(\text{V}^{0}_{\text{Cd}}\) as a “killer center” and demonstrates the potential impediment of this native defect species to the photovoltaic efficiency of untreated CdTe.

To quantify the effect of this recombination channel on CdTe solar cell performance, we calculate the trap-limited conversion efficiency (TLC), which incorporates the effects of both metastability and structural, and electronic defects. As depicted in the current–voltage curve in Figure 6c, we find that cadmium vacancies can significantly reduce the open-circuit voltage \(V_{\text{OC,TLC}} \approx 1.04 \text{ V}\), minority carrier lifetime \(\tau_{n} = 29 \text{ ns}\), and thus the maximum achievable photovoltaic efficiency from the ideal 32.1% to 26.7% (for intrinsic \(p\)-type CdTe processed under typical anneal temperatures of 600 °C in a Te-rich atmosphere, see Supporting Information, Section S8). Due to the large hole concentrations in the \(p\)-type compound, \(\text{V}^{0}_{\text{Cd,Te Dimer}}\) will be the dominant state under steady-state illumination, with electron capture by this defect species representing the rate-limiting step:

\[
R_{\text{Total}} \approx R_{n,\text{Te Dimer}}^{0} = n_{\text{V}^{0}_{\text{Cd,Te Dimer}}}/n_{\text{V}^{0}_{\text{Cd}}}
\]

Our prediction is a testament to the importance of Cl treatment, strategic impurity doping, and \(Cd\)-rich growth environments in the fabrication of high-efficiency CdTe devices, which contribute to the passivation and reduction of cadmium vacancy populations. Notably, the recent achievement of open-circuit voltages surpassing the 1 V threshold for CdTe solar cells by Burst et al. required a switch to an unorthodox strategy of \(Cd\)-rich growth conditions and group V anion doping, reducing the formation of \(\text{V}^{0}_{\text{Cd}}\) (and \(\text{Te}^{0}_{\text{Cd}}\)).

In conclusion, we reconcile several longstanding discrepancies between theoretical predictions and experimental measurements for CdTe, predicting both a single double-acceptor level and the \(C_{\text{V}}^{+}, \text{V}^{0}_{\text{Cd}}\) hole–polaron state for the cadmium vacancy in CdTe. An equilibrium population of cadmium vacancies can facilitate rapid recombination of electrons and holes, reducing the maximum achievable power-conversion efficiency under idealized conditions by over 5%, for untreated CdTe. These recombination kinetics primarily arise from both metastable vacancy structures and the Te dimer configuration of \(\text{V}^{0}_{\text{Cd}}\) which, in addition to producing negative-U behavior, leads to anharmonic carrier capture PESs. Importantly, these results demonstrate the necessity to include the effects of both metastability and anharmonicity for the accurate calculation of charge-carrier recombination rates in photovoltaic materials.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.1c00380.

Computational methods; supporting notes S1 and S2; Figures S1–S3 and Tables S1–S4, showing bandgap-corrected hybrid DFT functional; bulk electronic structure; vacancy bonding, structural, and electronic analysis, including; discrepancies in theoretical studies; carrier capture model, results, and analysis, experimental identification of tellurium dimerization; defect electronic densities of states; and chemical potentials (PDF)

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References