# Strain tuning of native defect populations: The case of Cu₂ZnSn(S,Se)₄

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Native defects are ubiquitous especially in compound semiconductors and dominate the properties of many materials. Applying first principles calculations, we propose a novel strategy to tune native defect populations in Cu₂ZnSn(S,Se)₄ which is an emerging photovoltaic absorber material. The formation of Cu vacancies ($V_{Cu}$), which are predicted to be shallower acceptors than Cu on Zn antisites ($Cu_{Zn}$), can be greatly promoted by compressive strain. Additionally, nonlinearities are found in the strain dependence of the $V_{Cu}$ formation energy. Both uniform and non-uniform strains may be present in physical samples implying probable variations in native defect concentrations. *© 2014 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4863076]

Cu₂ZnSn(S,Se)₄ (CZTSSe) is of current interest as a promising next-generation photovoltaic absorber, because it consists of non-toxic and earth abundant elements.[1–11] Doping and recombination in the CZTSSe absorber layer are believed to be largely determined by its native defects.[11] In its close relative, Cu(In,Ga)(S, Se)₂ (CIGSSe), Cu vacancies ($V_{Cu}$) are the dominant native defects and act as important shallow acceptors.[12–14] Experimentally, CIGSSe is in polycrystalline form with many native defects and deep centers.[15] $V_{Cu}$ may also form clusters with some deep centers, which passivates them by shifting their states away from mid-gap.[12–14] However, unlike CIGSSe, the dominant native defects in CZTSSe under many growth conditions are predicted to be $Cu_{Zn}$ antisites.[16] These are also acceptors but are relatively deeper than $V_{Cu}$, which can lead to reductions in open-circuit voltage ($V_{oc}$).[16] It has been recognized that the dominance of the deeper $Cu_{Zn}$ acceptor is a bottleneck to improve the power conversion efficiency of CZTSSe devices and therefore it is important to develop strategies to promote $V_{Cu}$ formation.

External strains can be an additional parameter to the typical chemical potentials and temperatures in order to intentionally control native defect populations and equilibrium.[17] Several theoretical and experimental works suggest that substitutional or interstitial dopant formation can be tuned by external strains in Si and group III-V or II-VI compound semiconductors.[18–26] Zhu *et al.* suggested that dopant incorporation can be enhanced significantly if the external strain is in the same direction as the dopant induced volume change.[22] External strains were also proposed to tune vacancy populations in Si.[27]

To understand the strain tuning of native defect populations, it is essential to understand the lattice volume changes and the lattice stress induced by the defects. Different types of defects may induce different volume changes to the lattice,[22] determined by the nature of lattice stress they induce.[24] The formation of vacancies would generally tend to shrink the lattice.[27] For substitutional defects and dopants, the volume changes are in accordance with the relative size differences between

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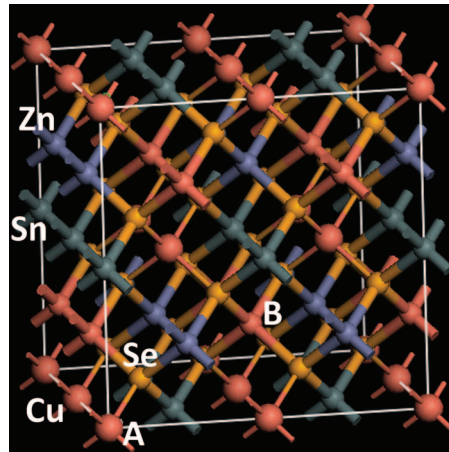
FIG. 1. Schematic illustration of the simulation supercell. (A and B are the crystallographically distinct sites of Cu.)

the defect or dopant atom and the host atom they replace, which includes an electronic contribution from the charge-state difference,[22] i.e., the quantum electronic stress (QES) effect.[24] For CZTSSe, the covalent radius of Cu and that of Zn are similar. However, because the valence of Cu is one electron less than Zn, a small volume contraction can be induced by $Cu_{Zn}$ due to the QES effect. On the other hand, $V_{Cu}$ is expected to induce a larger volume contraction than $Cu_{Zn}$. Consequently, the formation energy of $Cu_{Zn}$ (holding Fermi level and chemical potentials constant) is lower than that of $V_{Cu}$ and $Cu_{Zn}$ is the dominant native defect in CZTSSe.[16] For the same reason, if a compressive external strain is applied to the lattice, we may expect that $V_{Cu}$ formation should become more favorable compared to that of $Cu_{Zn}$. Therefore, in this letter, we propose that external compressive strain can be an effective means to promote $V_{Cu}$ and thus the hole concentration in CZTSSe. We have performed density functional theory calculations to verify this idea.

Our calculations were performed using the VASP code and the Perdew, Burke, Ernzerhof (PBE) generalized gradient approximation for the exchange-correlation potentials.[28] The core-valence electron interaction was treated using the projected augmented wave method.[29] We used a plane wave cutoff energy of 300 eV and a $4 \times 4 \times 4$ k-point mesh for sampling the Brillouin zone of a 64-atom supercell, as shown in Fig. 1. The convergence test of K-point sampling was performed. Total energy minimization was performed until the atomic forces converged to less than 0.01 eV/Å. The lattice of CZTSSe is kesterite[30] and our calculated lattice constants are a = 5.773 Å and c = 11.532 Å, which agree reasonably well with previous experimental and theoretical results and yield a unit cell volume $\Omega = 384.3$ Å$^3$.[16] We first calculated the volume change induced by $Cu_{Zn}$ and $V_{Cu}$. As a p-type dopant, $Cu_{Zn}$ is found to induce a small volume contraction of 6.91 Å$^3$ as expected from the hole-induced tensile lattice stress at the given doping concentration.[24] For Cu vacancies, there are two symmetry-distinct lattice sites (A and B) as shown in Fig. 1. Both sites generate similar volume contractions, 10.90 Å$^3$ for site A and 12.29 Å$^3$ for site B, which are larger than those induced by $Cu_{Zn}$ in alignment with qualitative predictions.

Next, we apply isotropic hydrostatic strains to the lattice by simultaneously changing the cell dimensions equally along x, y, and z directions. The $Cu_{Zn}$ formation energy may be calculated from

$$E_{CuZn,formation} = E_{CuZn} - E_{ref} + \mu_{Zn} - \mu_{Cu}, \qquad (1)$$

in which $E_{CuZn}$ is the total energy of the supercell with $Cu_{Zn}$, $E_{ref}$ is the total energy of the reference system, and $\mu_{Zn}$ and $\mu_{Cu}$ are the chemical potentials of Zn and Cu, respectively. To calculate the strain dependent contribution to the formation energy, we evaluate Eq. (1) in the strained and unstrained states and subtract them. This energy difference is plotted as a function of hydrostatic strain as triangles in Fig. 2 and is found to be super-linear. It favors compressive strains because Cu is slightly smaller than Zn and Cu has one fewer valence electron than Zn. The $V_{Cu}$ formation energy may be
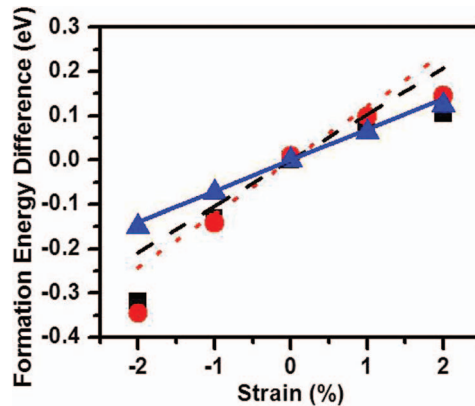
FIG. 2. Defect formation energy difference as a function of external hydrostatic strain. (Circle (red): $V_{Cu}$ at site B. Square (black): $V_{Cu}$ at site A. Triangle (blue): $Cu_{Zn}$. Solid line (blue): calculated $Cu_{Zn}$ formation energy difference by elastic theory. Dotted line (black): calculated $V_{Cu}$ formation energy difference at site A by elastic theory. Dashed line (red): calculated $V_{Cu}$ formation energy difference at site B by elastic theory.)

calculated as

$$E_{VCu, formation} = E_{VCu} - E_{ref} + \mu_{Cu}, \tag{2}$$

in which $E_{VCu}$ is the total energy with a Cu vacancy. Again, we calculate the strain dependent part of the formation energy by subtracting the total energies evaluated in strained and unstrained conditions. In the strain-free condition, the formation energy for site A is slightly lower than that for site B, because site A induces a smaller volume change. We took the formation energy for site A under the strain-free condition as the reference energy to calculate the formation energy differences of site A and site B, and the results are plotted as functions of the external hydrostatic strains as squares and circles in Fig. 2, respectively. Under a typical growth temperature of 900 K, a 2% compressive strain will largely increase the concentration of $V_{Cu}$ to about two orders of magnitude and increase the concentration of $Cu_{Zn}$ to about one order of magnitude. The formation energy for $V_{Cu}$ on site B is lower than that for site A under compressive strains because the volume contraction is larger for $V_{Cu}$ on site B. Conversely, the formation energy for site B is higher than site A under tensile strains. This indicates that external strains can change the relative formation energy of different defect formation sites. To verify that the transition energy level of $V_{Cu}$ is still shallow under compressive strains, we calculated the transition energy level of $V_{Cu}$ using Heyd, Scuseria, Ernzerhof (HSE) hybrid functional with the corrections of 1s core level of atoms far away from the vacancy. The method of the calculation followed Ref. [16]. The transition energy is insensitive to external strains. A 2% compressive strain increases the transition energy for 2 meV.

There is a significant difference between the strain dependent contributions to the formation energies of $V_{Cu}$ and $Cu_{Zn}$ because $V_{Cu}$ on either A or B sites generates a much larger volume contraction than $Cu_{Zn}$. Specifically, at 3% compressive strain, the formation energy difference of $V_{Cu}$ at site B is found to be 384 meV lower than that of $Cu_{Zn}$. This suggests that the formation of $V_{Cu}$ can be enhanced compared to $Cu_{Zn}$ by applying compressive strains to the lattice. Under the strain-free condition, the formation energy of $V_{Cu}$ was calculated to be about 360 meV higher than $Cu_{Zn}$ at a set of chemical potential of $\mu_{Cu} = -0.2$ eV, $\mu_{Zn} = -1.17$ eV, and $\mu_{Sn} = -0.62$ eV.[16] The above results suggest that a 3% compressive strain could favor the formation of $V_{Cu}$ over that of $Cu_{Zn}$, which would result in a higher concentration of shallower acceptors in the material. Quantitatively, this strain-dependent energy difference can result in variation of the concentration of $V_{Cu}$ by as much as two orders of magnitude at the typical growth temperature of 900 K. The Zn on Cu antisite is a compensating donor defect with formation energy in strain-free conditions only slightly higher than that of $V_{Cu}$.[16] $Zn_{Cu}$ will compensate any type of acceptors and can passivate $Cu_{Zn}$ acceptors by forming neutral complexes in CZTSSe. This mechanism may be desirable at higher concentrations of native acceptor doping because the depletion width should be kept similar

to the absorption depth for the solar spectrum. Under the same conditions of 3% compressive strain, we found that the formation energy of $Zn_{Cu}$ donors is made larger by 387 meV compared to the strain-free case, which would result in a similar two orders of magnitude reduction in concentration at 900 K. Therefore, compressive strain is simultaneously effective in both promoting the desired shallower native acceptor $V_{Cu}$ and in suppressing the undesirable compensation by $Zn_{Cu}$.

Our calculations show interesting deviations from simple elastic behavior. The strain-dependent defect formation energy can be understood from elastic theory:

$$E_d = \int \Omega \sigma (\varepsilon) d\varepsilon, \tag{3}$$

in which $\sigma(\varepsilon)$ is the defect induced stress in an unstrained lattice. The lattice stress induced by $V_{Cu}$ at site A, site B and by $Cu_{Zn}$ are calculated to be 2.62, 2.18, and 1.57 meV/Å$^3$, respectively. They are the physical origins that determine the physical trend of the strain induced volume change shown above, in terms of both sign and magnitude of change. For small external strains, the strain-dependent defect formation energy can be expressed as

$$E_d = 3\Omega \sigma (0) \varepsilon. \tag{4}$$

Therefore, to the first-order approximation, the slope of the defect formation energy vs. strain curve could be determined directly by the sign and the magnitude of the defect induced the stress under the strain-free condition, as shown in Fig. 2. Our calculations show that this approximation applies to the curve of $Zn_{Cu}$ quite well. However, it is clear from Fig. 2 that the dependence of the formation energy of $V_{Cu}$ on strain is not linear. This is because, strictly speaking, linear elastic theory applies to elastic deformation that preserves lattice symmetry. For Cu vacancy formation, there is a large local lattice relaxation for atoms around the Cu vacancy that breaks the lattice symmetry adding bond angle changes, and as a result, the linear elastic theory works less well.

Nonuniform strains of 3% may be found within polycrystalline films on foreign substrates, for example, at grain boundaries as a result of growth and cooling; thus our result suggests that the doping by native defects may not be spatially uniform in most samples. It may also be possible to intentionally subject films to biaxial or uniaxial strain states by epitaxial growth. Experimentally, compressive strain can be observed in thin films of CZTS(Se) due to thermal expansion mismatch with the underlying Mo and substrate.[31] Therefore, we also calculated the strain-dependent $V_{Cu}$ and $Cu_{Zn}$ formation energies for uniaxial (along c axis) and the biaxial strains. First, we applied uniaxial strains from 2% to $-2$%, and repeated the defect formation energy calculations. The calculated formation energy differences for $V_{Cu}$ and $Cu_{Zn}$ vs. the uniaxial strains are shown in Fig. 3(a). The general trend is about the same as the case of the hydrostatic strain. Both $V_{Cu}$ and $Cu_{Zn}$ favor compressive strains. Compressive uniaxial strains reduce the $V_{Cu}$ formation energy more than $Cu_{Zn}$. At a 2% compressive uniaxial strain, the formation energy difference between the $V_{Cu}$ and $Cu_{Zn}$ is reduced to approximately 17 meV, which is much smaller than the difference under a 2% hydrostatic strain. This is because the uniaxial strain induces a much smaller lattice deformation than hydrostatic strain. Also, uniaxial strains are anisotropic and thus site A is always the favorable site for $V_{Cu}$ formation under any uniaxial strains along the c direction.

Next, we applied biaxial strains from 2% to $-2$%, and repeated the defect formation energy calculations. The calculated $V_{Cu}$ and $Cu_{Zn}$ formation energy differences vs. the biaxial strains are shown as Fig. 3(b). Again, the general trend is similar and the formation energies of both $V_{Cu}$ and $Cu_{Zn}$ are favored by compressive strain; however the effects on $V_{Cu}$ formation energies are greater than for the $Cu_{Zn}$ antisite. At a 2% compressive biaxial strain, the formation energy difference between the $V_{Cu}$ and $Cu_{Zn}$ is about 33 meV, which is smaller than the case of the hydrostatic strain but larger than the case of the uniaxial strain, as expected. One difference is that under a compressive biaxial strain, $V_{Cu}$ at site B is stable and under a tensile biaxial strain, $V_{Cu}$ at site A is stable.

In conclusion, we demonstrate a possible strategy to promote the $V_{Cu}$ against $Cu_{Zn}$ in CZTSSe by building in or applying hydrostatic, uniaxial, or biaxial compressive strains. At a 3% hydrostatic strain, we expect the $V_{Cu}$ to become the dominant native defect in CZTSSe. At the same time, the formation of $Zn_{Cu}$ can be greatly suppressed. We also note that the change to the formation energy of vacancies was found to deviate from simple linear elastic theory, which is attributable to bond angle changes. Our calculations suggest that strain engineering can be an effective approach to tune the
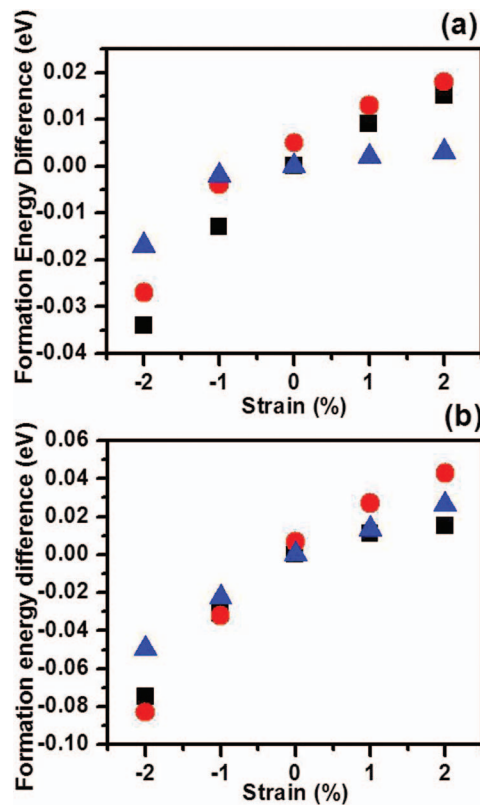
FIG. 3. (a) Defect formation energy difference as a function of external uniaxial strain. (b) Defect formation energy difference as a function of external biaxial strains. (Circle (red): $V_{Cu}$ at site B. Square (black): $V_{Cu}$ at site A. Triangle (blue): $Cu_{Zn}$.)

native defect populations in semiconductors, and we expect the approach to be generally applicable to many other material systems.

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