Supporting Information for

Silicon As an Unexpected n-Type Dopant in BiCuSeO Thermoelectrics

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In this work, the Vienna Ab initio Simulation Package (VASP) was used to carry out the density functional theory (DFT) calculations[1-3]. The DFT + U method was adopted due to the exchange-correlation effects of the strongly localized Cu 3d electrons. The effective Coulomb parameter U was set to 4 eV based on the study of Zhang et al[4]. The parameterization by Perdew, Burke, and Ernzerfhof (PBE) based on the generalized gradient approximation (GGA) [5] with projector augmented wave (PAW) method was applied to calculate the electronic structures.

We employed a 9×9×4 k-point mesh[6] generated by the Monkhorst-Pack scheme for numerical integrations over the Brillouin zone of the tetragonal unit cell that contains eight atoms in total with two atoms for each component. A 3×3×1 supercell containing 72 atoms was constructed with its Brillouin zone sampled with a 3×3×4 k-point mesh. The plane wave cutoff energy was set to 500 eV and atomic coordinates were relaxed until the total energy converged to 10^{-5} eV. The semiclassical Boltzmann transport theory implemented in BolzTraP[7] was applied to calculate the electrical transport properties. A denser k-point mesh of 9×9×12 was utilized for the 3×3×1 supercell for accurate transport property calculations.

Effective band structures of doped BiCuSeO were recovered from supercell calculations using the band unfolding technique proposed by Medeiros et al[8, 9]. The spectral weight $P_{\vec{K}m}(\overrightarrow{k_\iota}) = \sum_n \left|\langle \vec{K}m|\overrightarrow{k_\iota}n\rangle\right|^2$ was calculated to unfold the band structures, where $P_{\vec{K}m}(\overrightarrow{k_\iota})$ is the probability of finding a set of primitive cell states $|\overrightarrow{k_\iota}n\rangle$ contributing to the supercell states $|\vec{K}m\rangle$[10].

Due to the restrictions of band unfolding technique, only partial relaxations of atomic coordinates are possible. As can be seen from Fig. S1, full relaxations including lattice parameters lead to negligible differences in the formation energies and electronic structures from partial relaxations.

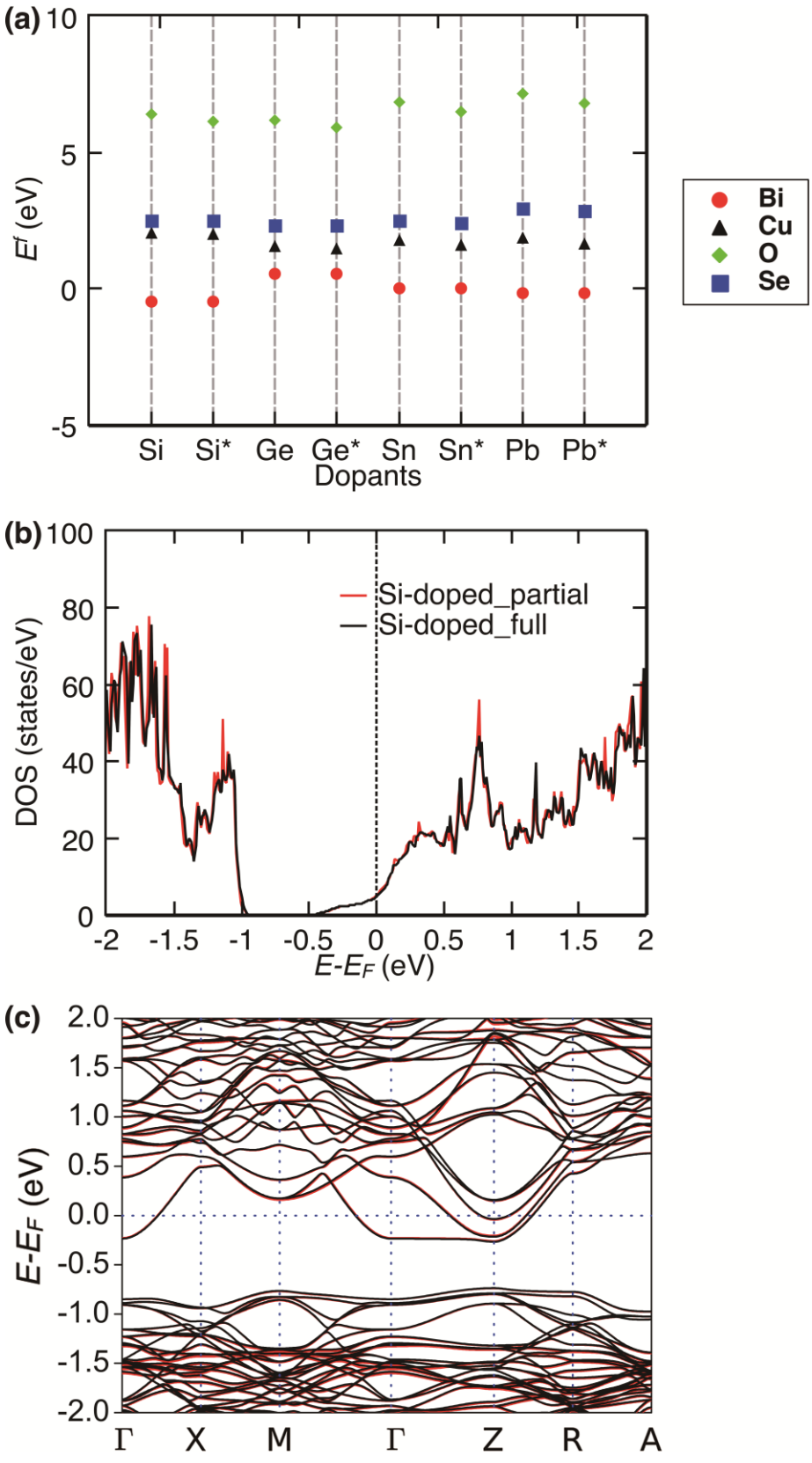

Figure S1 (a) Formation energies of doped BiCuSeO calculated from DFT. Atomic symbols with and without a star superscript represent full and partial relaxations, respectively. (b) DOS and (c) band structures of Si-doped BiCuSeO with full and partial relaxations.

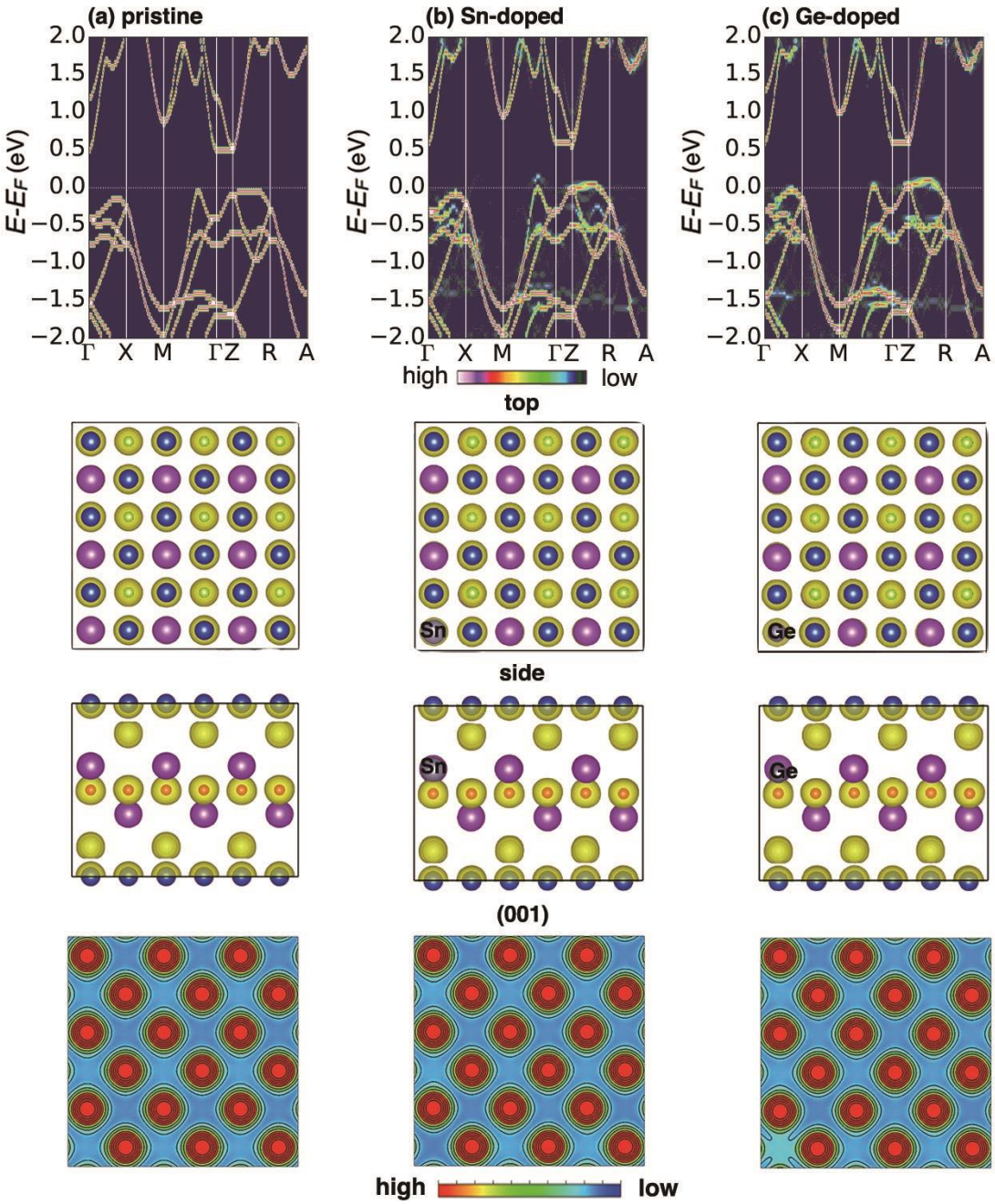

Figure S2 Effective band structures and charge density distributions of (a) pristine, (b) Sn-doped and (c) Ge-doped BiCuSeO. The (001) plane crosses the oxygen atomic layer in BiCuSeO. Fermi level is located at 0 eV. The isosurface level is 0.12 e/Å^3.

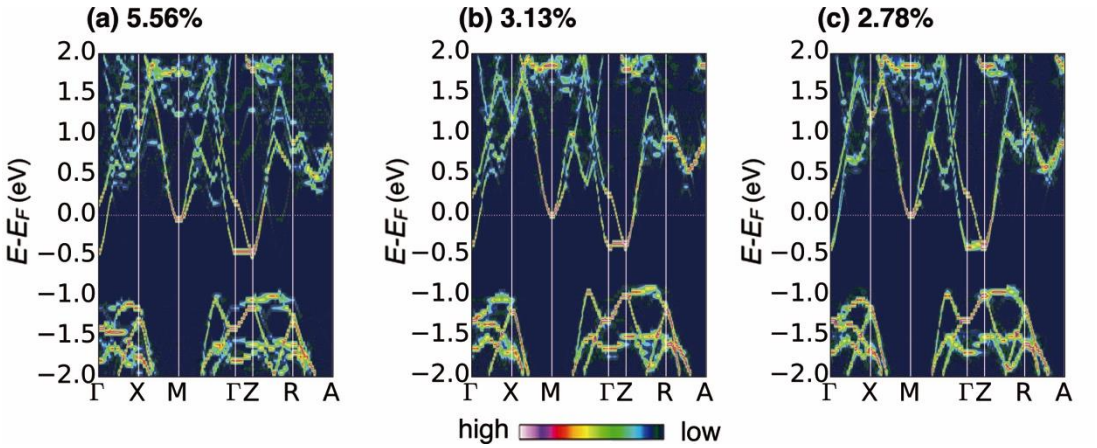

Figure S3 Effective band structures of BiCuSeO with (a) 5.56%, (b) 3.13% and (c) 2.78% Si doping concentrations. Fermi level is located at 0 eV. It is seen that the n-type behavior is insensitive to the doping concentration.

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