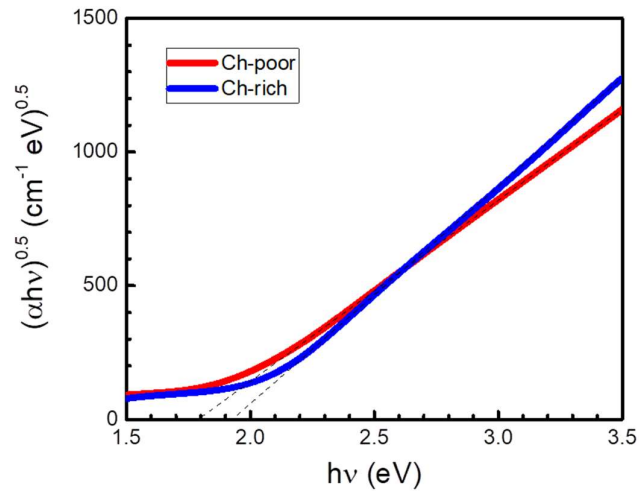


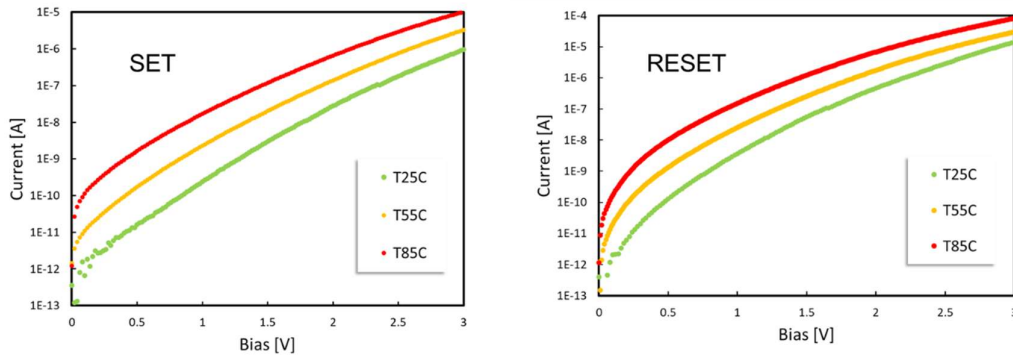
SUPPLEMENTARY INFORMATION

alloy	Se (atom %)	Band gap (eV)
ch-rich	64	1.92
ch-poor	54	1.8

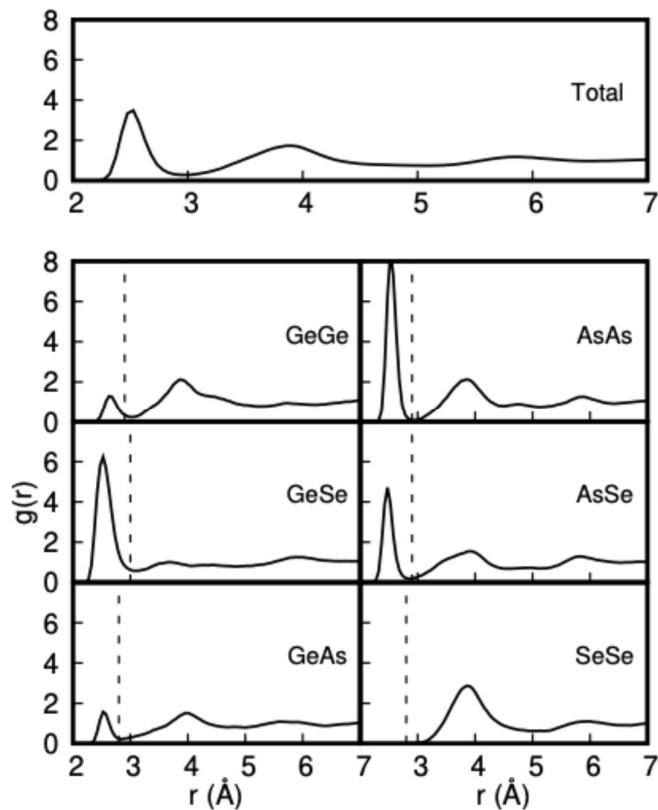
Supplementary Table 1. Bilayer stack: chalcogen composition content (at. %) and corresponding optical bandgap (from absorption spectra reported below).



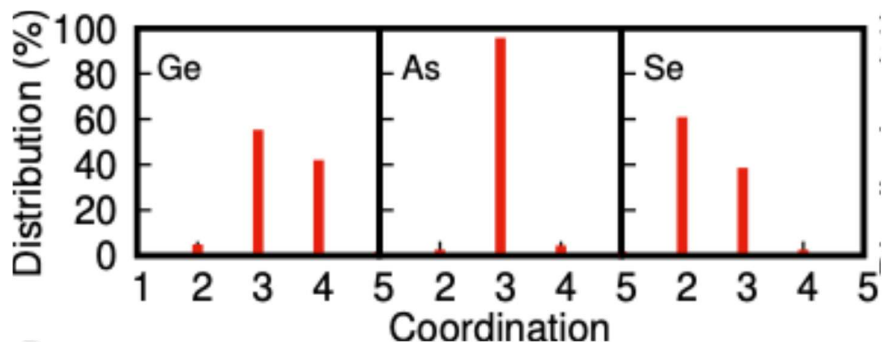
Supplementary Figure 1. Tauc plot for Ch-poor and Ch-rich films. The linear extrapolation (dashed lines) provides the Tauc band gap.



Supplementary Figure 2. I - V characteristics at various temperatures collected from the bi-layered chalcogenide capacitor by changing the polarity to mimic the SET (on the left) and RESET (on the right) states of a hypothetical segregated cell. The activation energy is obtained as $E_A = -\frac{\partial \log I}{\partial (1/kT)}$ [1].



Supplementary Figure 3. Partial and total pair correlation functions of amorphous GAS234 (a-GAS234) at 300 K averaged over four independent 300-atom models. The vertical lines indicate the cutoff used to compute the coordination numbers.



Supplementary Figure 4. Distribution of coordination numbers for the different species, averaged over four a-GAS234 models.

	Ge	As	Se	Total
Ge	0.28	0.32	2.78	3.38
As	0.27	1.46	1.29	3.02
Se	1.54	0.86	0.00	2.40

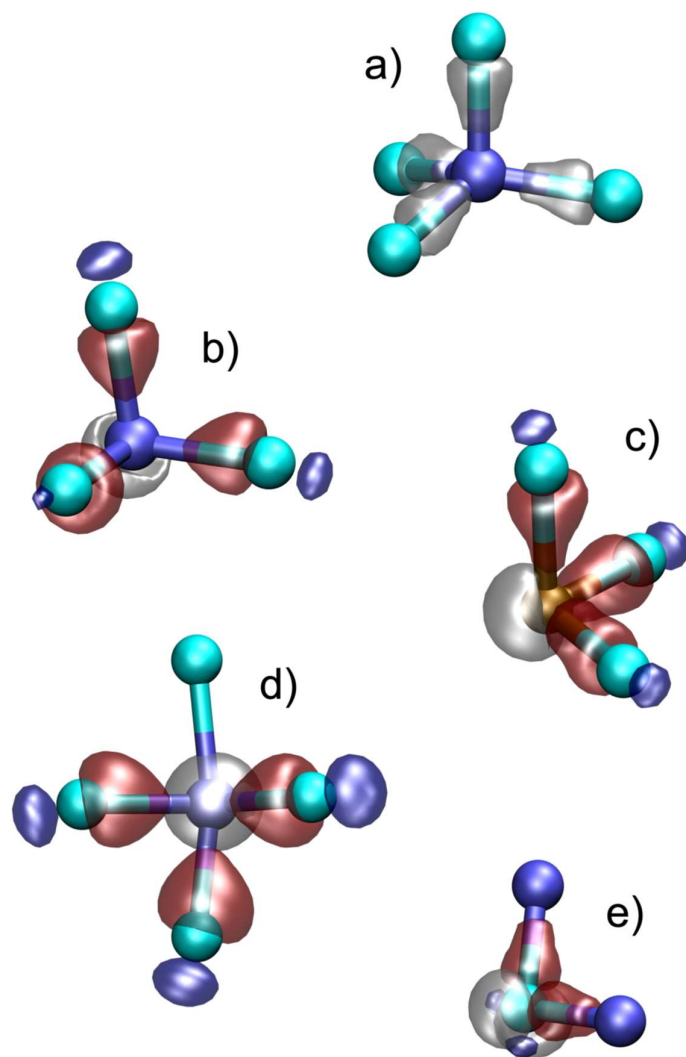
Supplementary Table 2. Distribution of the partial coordination numbers averaged over four a-GAS234 models.

	AsSe	GeSe	AsAs	GeAs	GeSe	GeGe
%	27	49	15.5	5.7	0.0	2.5

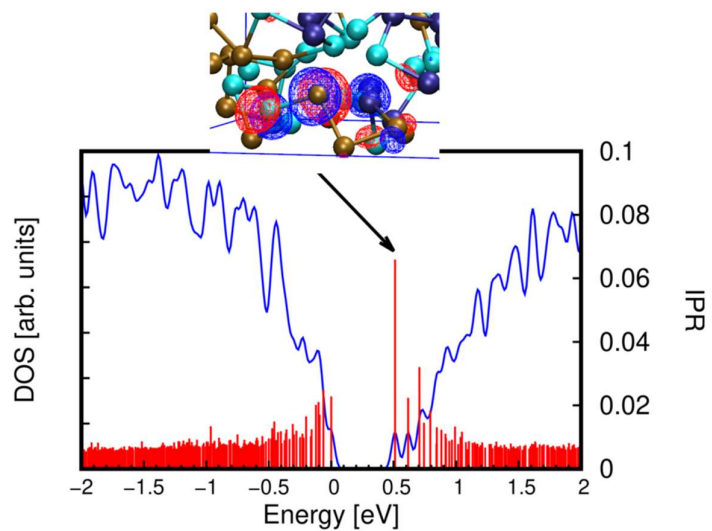
Supplementary Table 3. Percentage of the different types of bonds averaged over four a-GAS234 models.

	Ge _t	isolated Ge _t	Corner-sharing Ge _t	Edge-sharing Ge _t
%	33	60	35	4

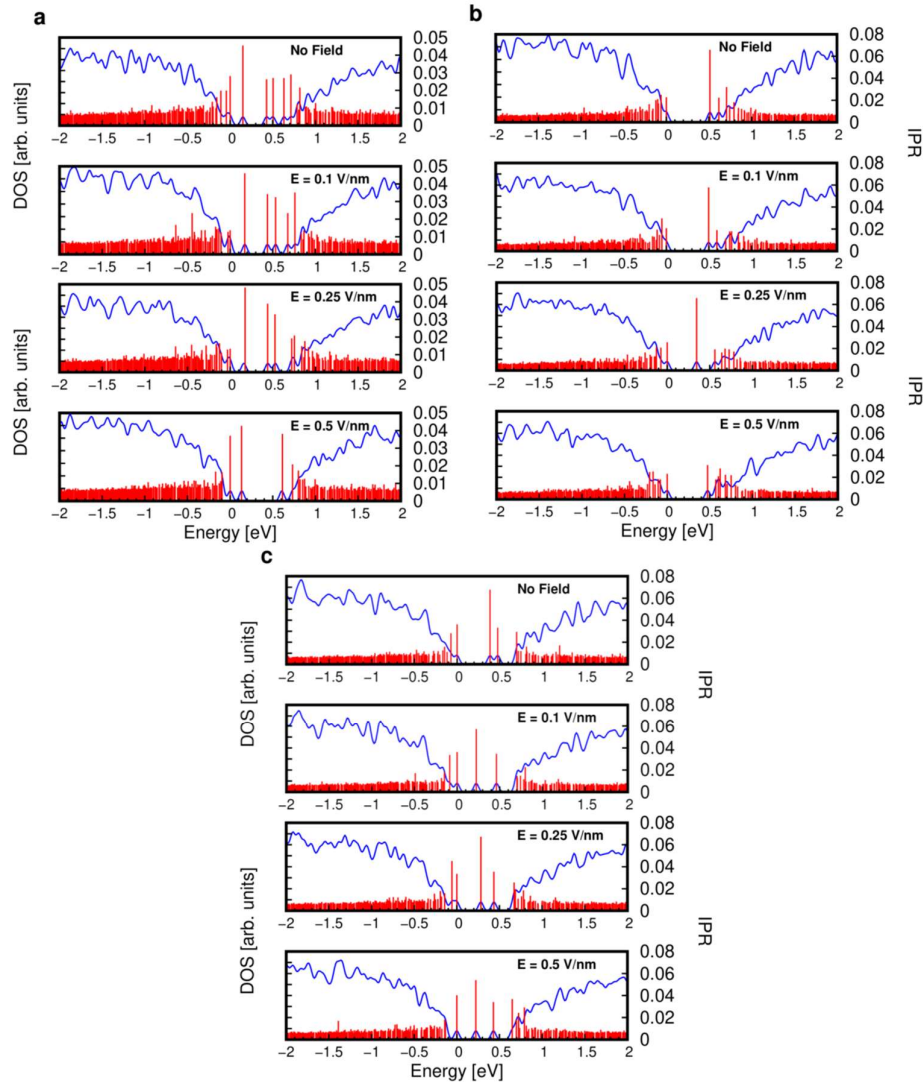
Supplementary Table 4. Percentage of Ge atoms in a tetrahedral environment (Ge_t) with respect to the total number of Ge atoms, and percentage of isolated, corner- and edge-sharing tetrahedra. Isolated means that the tetrahedron does not share vertices with other tetrahedra. The data are averaged over four independent models. The Ge atoms in a tetrahedral environment was computed from the order parameter for tetrahedrality introduced in Ref. [2] and used in our previous works on amorphous tellurides [3].



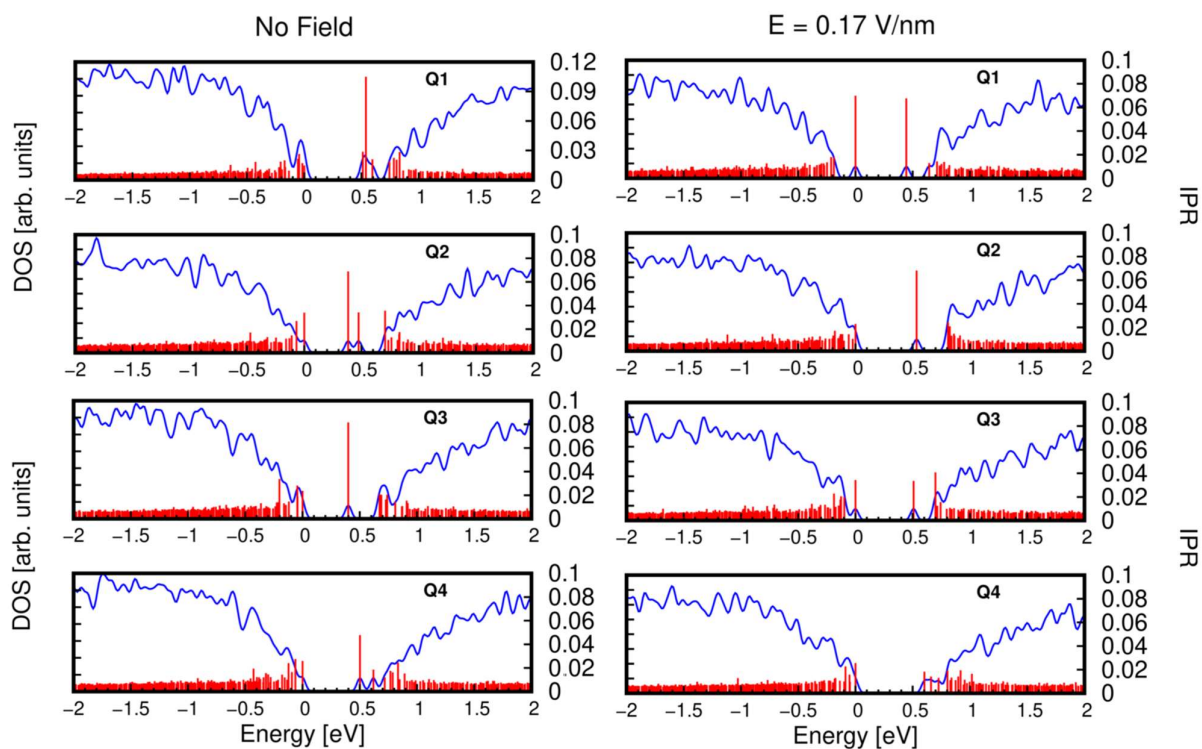
Supplementary Figure 5. Isosurface of Wannier functions (WF) for different atomic environments in the models of a-GAS234. WFs are the periodic version of the occupied Boys orbitals obtained by the unitary transformation of the Kohn-Sham occupied orbitals, which minimizes the quadratic spread [4]. a) Ge in a tetrahedral site, b) Ge and c) As in a pyramidal bonding geometry, d) Ge in defective octahedra with coordination four and e) Se two-coordinated. The pyramidal geometry of three-coordinated Se is the same of that of panel c). The atomic color code is the same as in Figure 6a in the article. Iso-surfaces with different colors (red and blue) have different sign. Wannier functions with spherical iso-surfaces (gray) are s-type lone pairs.



Supplementary Figure 6. Electronic density of states (DOS) and inverse participation ratio (IPR) of model M1 of a-GST234. The zero of energy corresponds to the highest occupied state (top of the valence band or highest occupied molecular orbital, HOMO). The DOS is computed from KS energies at the supercell Γ -point with a 27 meV Gaussian broadening. The iso-surface of an in-gap localized electronic state (lowest unoccupied molecular orbital, LUMO) is highlighted in the inset. Iso-surfaces with different colors (red and blue) have different sign. The LUMO is localized over a chain of wrong As-As and As-Ge bonds (As-Se-As-As-As-Ge chain, see Figure 6a for the color code on atoms).



Supplementary Figure 7. Electronic density of states (DOS) and inverse participation ratio (IPR) of model a) M3 b) M1 c) M2 of a-GST234. The models are relaxed with no field or with an electric field and then further relaxed by removing the field. The strength of the field is given in the insets. The zero of energy always corresponds to the highest occupied Kohn-Sham state (highest occupied molecular orbital, HOMO). In model M3 (panel a) no sizable changes are observed with a field up to 0.25 V/nm. At 0.5 V/nm we observed instead a dramatic change of the in-gap states, the lowest unoccupied molecular orbital (LUMO) is now close to the valence band and the LUMO+1 is close to the conduction band. However, these two states are not related to the LUMO and LUMO+1 states of the original model. The LUMO is now localized on an As-As-As-Ge chain while the LUMO+1 is now localized on a GeSe₄ group with a tetrahedral Ge atom. Therefore, a large electric field leads to the removal of deep defect states in the gap in model M3. In model M1 (panel b), one observes a slight shift to lower energy of the LUMO state for a field strength up to 0.25 V/nm. This state is localized on an As-Se-As-As-As-Ge chain (see article). At the highest field of 0.5 V/nm, the LUMO and LUMO+1 states which were originally localized of neighboring chains of wrong bonds mix to some extent. The LUMO moves to a position in energy closer to the original one, but a few other localized states at the edge of the conduction band move to slightly lower energy. In model M2 (panel c), the LUMO state does not change sizably with the field up to 0.25 V/nm. At 0.5 V/nm, the LUMO shifts close to the valence band by keeping the same character (it is localized on a Se₃Ge-Ge group). The HOMO state changes instead its character, and it lifts off the valence edge.



Supplementary Figure 8. Electronic density of states superimposed to the IPR for the four models Q1-Q4 equilibrated at 500 K with (right panels) and without (left panels) the electric field 0.17 V/nm large. All the models were then quenched at 300 K and finally relaxed at zero temperature without the electric field and the DOS are computed without the electric field as well. The zero of energy always corresponds to the highest occupied Kohn-Sham state (highest occupied molecular orbital, HOMO).

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