# Supporting Information

## The surface passivation of Ge(100) and Ge(111) anodes in Ge-air batteries with different doping types and concentrations

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## Method

The calculation of the electrostatic potential difference, projected local density of states (PLDOS) is based on the $Ge/GeO_2$ device. The exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) was used for the GGA calculations. The mesh cut-off was 125 Ha and a $4 \times 4 \times 1$ k-point mesh was used. The Green's function surface model consisting of a single surface region attached to an electrode (a fully periodic bulk) was used. The electronic structure is matched at the electrode-surface boundary using Green's functions. The temperature of the electrode was 300 K. The energy range of PLDOS was -2.5 ~ 1.5 eV with 101 points.

The calculation of the transmission spectra and IV curves are based on the $Ge/GeO_2/Ge$ device. The exchange-correlation functional of Perdew-Burke-Ernzerhof (PBE) was used for the GGA calculations. The mesh cut-off was 125 Ha and a $4 \times 4 \times 150$ k-point mesh was used. The voltage bias was 0 ~ 1 V with 11 points and the energy range was -6 ~ 6 eV with 601 points.

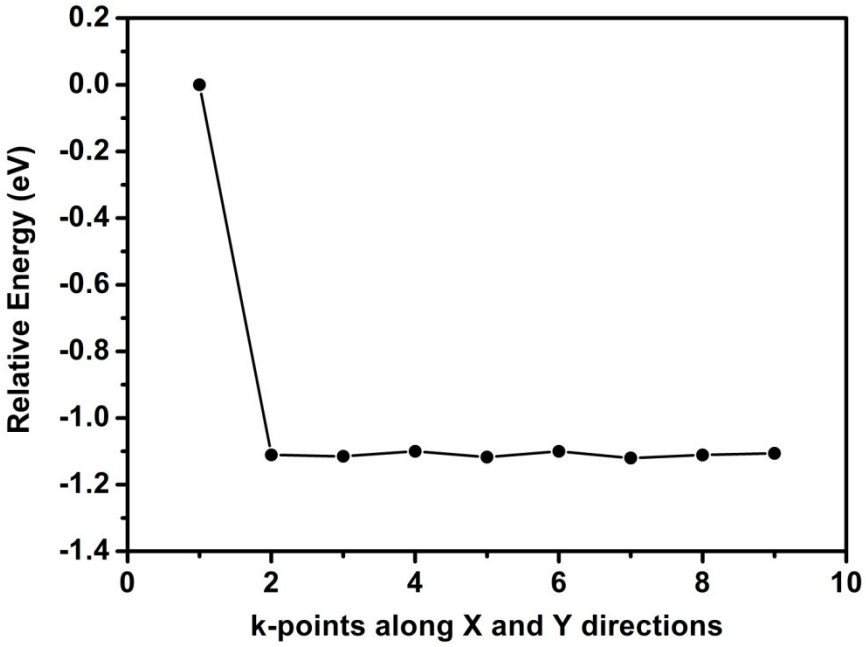


**Figure S1.** The calculated relative binding energy of Ge(100)/$GeO_2$ interface with the k-points varying from 1×1×1 to 9×9×1.

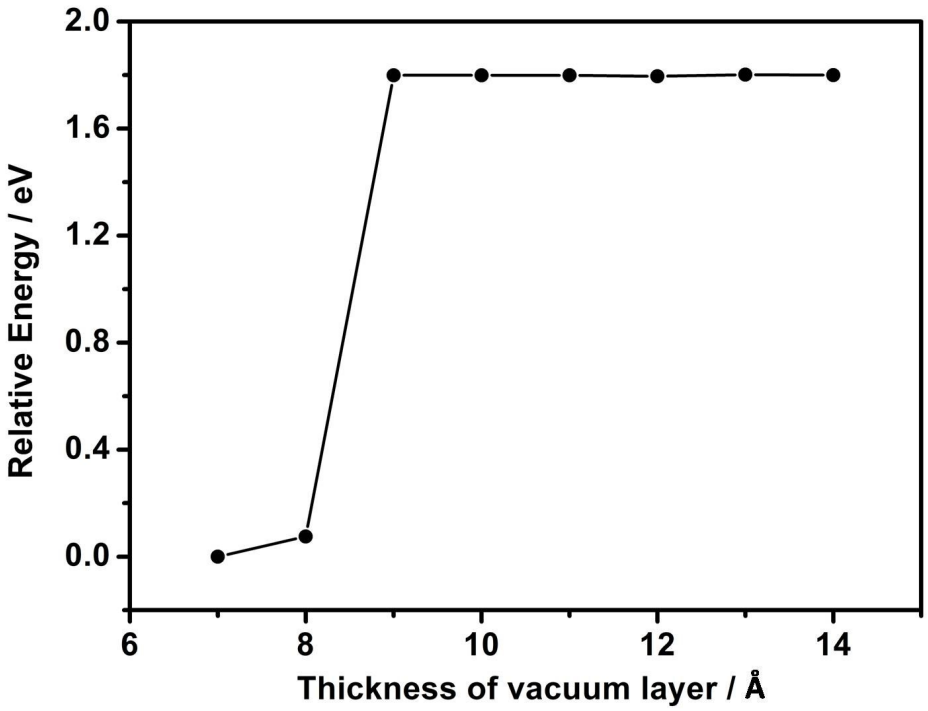


**Figure S2**. The calculated relative energy of Ge(100)/$GeO_2$ interface with the thickness of the vacuum layer varying from 7 to 14 Å.

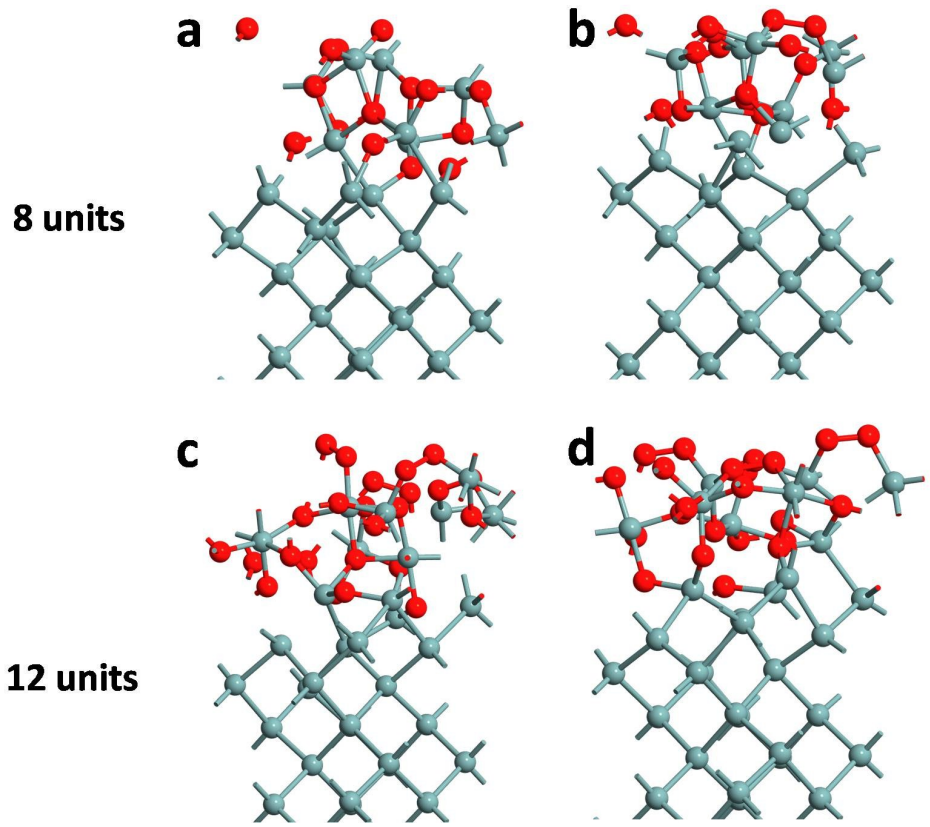


**Figure S3**. Atomic configurations of Ge(100)/$GeO_2$ interfaces with 8 units $GeO_2$ (a and b) and 12 units $GeO_2$ (c and d). The configurations in figure b and d have an O vacancy.

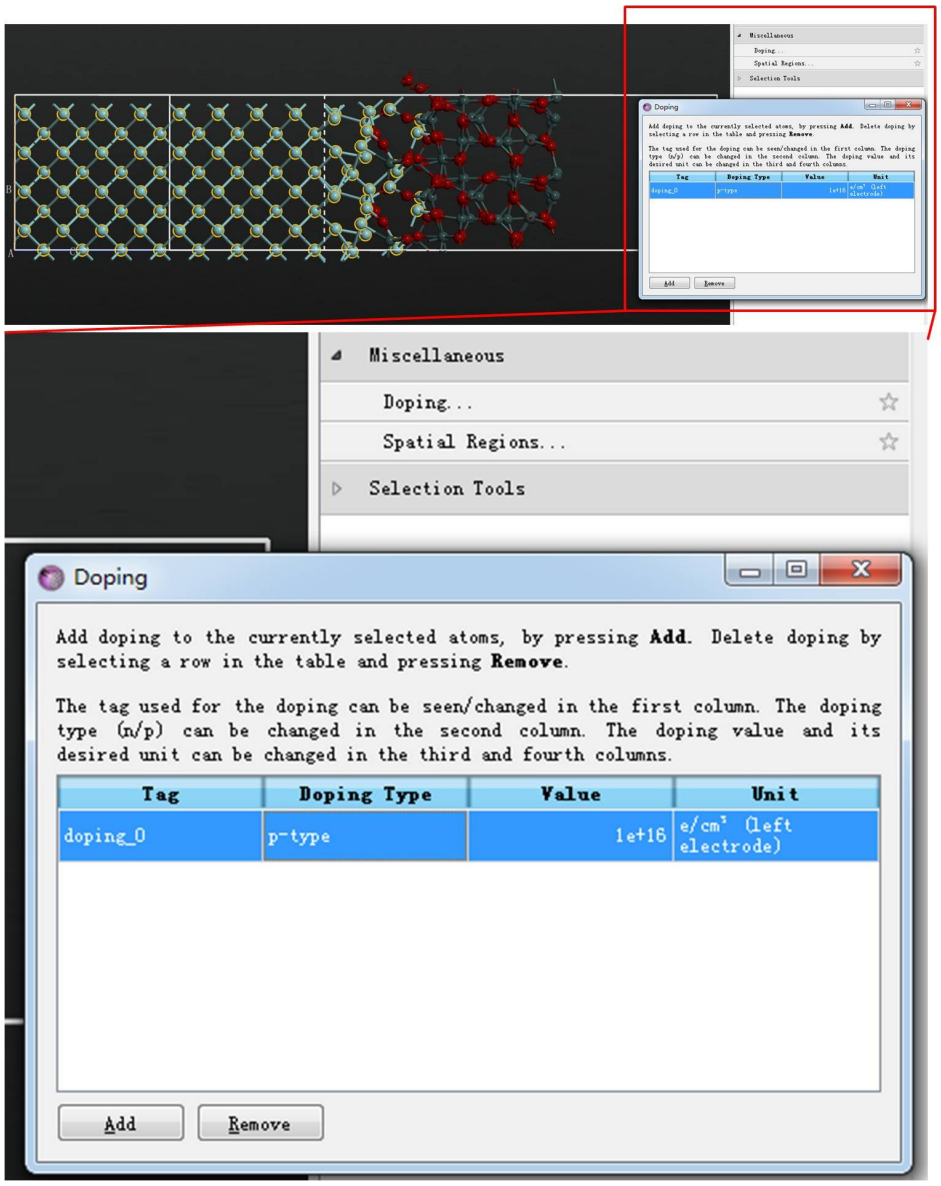


**Figure S4**. The screen captures of the "Doping" panel in the Atomistix Toolkit (ATK) code from QuantumWise.

The doping concentration was controlled by the "Doping" panel in the Atomistix Toolkit (ATK) code from QuantumWise. "Doping" adds doping charge with different types and values to the group of currently selected atoms like Ge, which are highlighted in the $Ge/GeO_2$ configuration. This tool is of particular interest to modelling of doping effect in an atomistic semiconductor device conveniently without explicitly introducing dopant atoms.

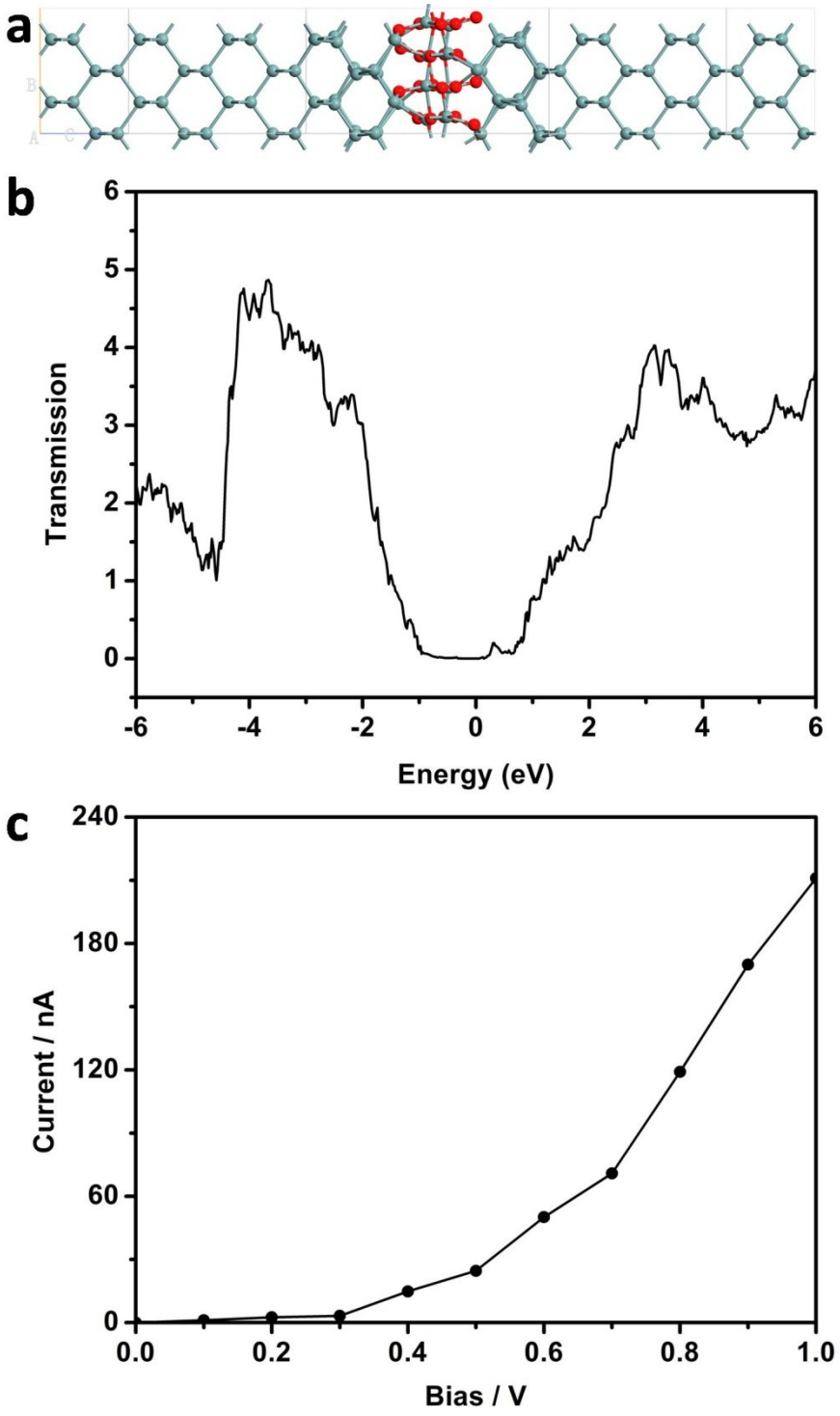


**Figure S5**. (a) Atomic configurations of the Ge(100)/$GeO_2$/Ge(100) devices with oxygen vacancies; (b) The k-point averaged transmission spectra of Ge(100)/$GeO_2$ interfaces with oxygen vacancies as function of energy; (c)The I-V curves of Ge(100)/$GeO_2$ interfaces with oxygen vacancies.