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The effects of uniaxial and biaxial strain on the electronic structure of germanium

Kaoruho Sakata [a,*], Blanka Magyari-Köpe [a,*], Suyog Gupta [a], Yoshio Nishi [a], Anders Blom [b], Peter Deák [c]

[a] Department of Electrical Engineering, Stanford University, Stanford, CA 94305, USA
[b] QuantumWise A/S, Fruebjergvej 3, 2100 Copenhagen, Denmark
[c] Bremen Center for Computational Materials Science, Universität Bremen, Bremen, Germany

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ABSTRACT

The effects of uniaxial and biaxial strain on the electronic structure of bulk germanium are investigated using density functional theory in conjunction with four approximations for the exchange correlation interaction: the local density approximation (LDA) and generalized gradient approximation (GGA) with on-site Hubbard corrections (LDA+*U*, GGA+*U*), the meta-GGA (MGGA), and the screened hybrid functional (HSE06). The band structure and, especially, the band gap of unstrained Ge are well reproduced by these methods. The results of LDA+*U*/GGA+*U* and MGGA show that a biaxial tensile strain above 1.5% turns Ge into a direct-gap (Γ–Γ) semiconductor, whereas the indirect Γ–L gap is maintained for uniaxial strain up to 3%. The HSE06 results confirm a similar trend, although the predicted critical strain is lower. The effective masses were also calculated and they were found to be in good agreement with experiments for bulk Ge. It is predicted that the masses at Γ can be tuned to be smaller/larger by tensile/compressive strain in all directions.

1. Introduction

Strain engineering is a powerful tool that can be used to achieve significant improvements in device performance. Germanium has been under intense investigation lately as a promising material for optoelectronic applications and complementary metal–oxide–semiconductor (CMOS) field-effect transistor devices. Strained Ge can exhibit enhanced light emission efficiency as well as improved electron transport characteristics for both electrons and holes, depending on the crystal orientation and strain [1–3]. Previous experimental and theoretical studies have indicated the possibility that the energy separation between the direct and the indirect valleys in Ge can be reduced by the application of tensile strain, which is a similar phenomenon to that exhibited by strained Si [4–6]. It has been theoretically predicted that Ge becomes a direct-band-gap material under biaxial tensile strain of about 1.7%, because the energy of the lowest conduction band state in the direct valley (Γ) shifts downward more rapidly than the states at L [1]. Biaxial tensile strain also induces an increase of the electron population at Γ, leading to an enhancement of the radiative recombination via direct transitions [7,8]. Tensile-strained nanomembranes have been fabricated and shown to indeed improve the light emission efficiency of Ge; they have also been studied for implementation as light-emitting diodes [9,10], lasers [11], and photodetectors [12] using several fabrication methods. Therefore, the development of a scalable band-structure prediction framework that can accurately predict the strain dependence of the electronic properties of Ge is of vital importance for optoelectronic and CMOS applications because strain has been found to enhance both the electron and hole transport properties of Ge [13,14]. The theoretical framework must be able to deliver accurate predictions of all the properties of Ge under applied strain, but also be scalable up to 1000 or more atoms to enable studies of strained Ge interfaces with oxides and metals, as well as in supercells with impurities and grain boundaries. The latter requirement strictly excludes approaches like *GW*, which can provide highly accurate band structures of Ge [15–17] (especially if core polarization is included [16]), but only at a very large computational cost already for the primitive crystal cell.

Owing to the electron self-interaction error, standard local and semi-local approximations (local density approximation (LDA), generalized gradient approximation (GGA)) to the density functional theory (DFT) predict Ge to be a metal. Therefore, to reproduce the semiconductor gap (and to provide a reasonable first guess of the equilibrium geometry and corresponding wave

* Corresponding authors. Tel.: +1 650 725 5725; fax: +1 650 725 0991.
E-mail addresses: ksakata@stanford.edu (K. Sakata), blankamk@stanford.edu (B. Magyari-Köpe).

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functions for *ab initio* many-body methods), two semi-empirical methods can be used: the application of on-site Coulomb parameters (U) in standard DFT [18] or mixing the Hartree–Fock (HF) exchange with GGA in the framework of the generalized Kohn–Sham theory. The screened hybrid functional (HSE06) is such a hybrid functional, in which the screening of the exact exchange has also been considered [19–21]. HSE06 has been shown to successfully correct for the electron self-interaction error (by error compensation between the HF and GGA exchange, providing a total energy that is a linear function of the fractional occupation numbers) and to reproduce well both the ground state properties and the band gaps for group IV semiconductors [22]. Meta-GGA (MGGA) functionals were also designed to reproduce the shape of the exact exchange potential of atoms by introducing an additional term in the exchange-correction potential that also takes into account the kinetic energy density. While most MGGA functionals are not capable of geometry optimization, they have provided improved band gaps for several insulator and semiconductor materials, including Si and Ge [23].

This study has two objectives. The first one is to validate the LDA+U/GGA+U approach for calculating the strain dependence of the electronic structure of Ge, both for uniaxial and biaxial strain. For this purpose, their results are compared to those of the two methods above them in Perdew's hierarchy [24,25], MGGA and HSE06, and to earlier calculations and available experimental results. The band structure of strained Ge has been previously calculated by Kotlyar *et al.* [26] using a tight-binding $sp^3d^5s^*$-SO Hamiltonian. Tahini *et al.* [27] used a simple GGA+U approach with $U = -3.33/2$ eV for both s and p states. In our study, we instead employ a scheme where separate U-values are specified for the p and d states. The second objective of the study is to predict the strain dependence of the effective mass. We show that all our methods can calculate the effective mass of bulk non-strained Ge in good agreement with experimental results, and we predict the effective mass of the examined strained structures.

2. Computational details

Our LDA+U/GGA+U calculations were performed with norm-conserving pseudopotentials using the Atomistix Toolkit (ATK) code from QuantumWise [28]. For the GGA calculations, the exchange–correlation functional of Perdew–Burke–Ernzerhof [29] was used. The program employs a localized numerical basis and allows the simultaneous variation of U on orbitals with different angular momenta. The values of U_p and U_d were chosen to reproduce the band gaps of unstrained Ge to within 0.05 eV of the experimental values [30] while simultaneously maintaining the reproduction of the ground state properties. In the case of the LDA+U calculations, split p-orbitals were applied (based on the split-valence method [31], which is widely used in quantum chemistry) with different U_p values.

The HSE06 calculations were performed using the projector augmented wave (PAW) method [32], as implemented in the Vienna Ab initio Simulation Package (VASP) [33–35], with standard mixing (25%) and screening (0.2 Å^{-1}) parameters. An energy cutoff of 420 eV was used in the plane-wave expansion, and the convergence criteria were set to 10^{-5} eV for the energy and to 10^{-2} eV/Å for the forces.

In the LDA+U/GGA+U and in the HSE06 calculations, the Brillouin zone of the primitive unit cell was sampled with a $10 \times 10 \times 10$ Monkhorst–Pack set [36] of k-points (including the Γ point).

The MGGA calculations were performed with the method of Tran and Blaha (TB09) [37] and the ATK package, using $21 \times 21 \times 21$ k-points and a localized basis with 4s, 4p^3, 5s, and 4d orbitals. The pseudopotential was taken from Hartwigsen–Goedecker–Hutter [38]. The inclusion of the 4d orbitals is essential; with a smaller basis set, it was found not to be possible to obtain a proper ordering of the conduction band minima.

According to Ref. [22], the spin–orbit interaction has been neglected in all our calculations.

To calculate the energy and electronic states of strained Ge after an initial structure optimization, uniaxial or biaxial strain was induced along the 1 0 0 direction in the range of −3% (compressive) to 3% (tensile). Experimental values of the compliance coefficients (c_{11} = 129.2 GPa, c_{12} = 47.9 GPa and c_{44} = 67.0 GPa) were used [39,40]. For the biaxial strain in the [1 0 0] direction, the corresponding strain tensors can be determined as follows:

$$\varepsilon_{[100]} = \begin{pmatrix} s_{11} & 0 & 0 \\ 0 & s_{12} & 0 \\ 0 & 0 & s_{12} \end{pmatrix} \cdot P \tag{1}$$

Here, s denotes the stiffness tensors, with components

$$s_{11} = \frac{c_{11} + c_{12}}{c_{11}^2 + c_{11}c_{11} - 2c_{12}^2} \tag{2}$$

$$s_{12} = -\frac{c_{12}}{c_{11}^2 + c_{11}c_{11} - 2c_{11}^2} \tag{3}$$

obtained from the relation $s = c^{-1}$. Moreover, the out-of-plane biaxial strain tensor component ε_{33} becomes

$$\varepsilon_{33} = \frac{-2c_{12}}{c_{11}}\varepsilon_{//} \tag{4}$$

When the in-plane strain tensor components (ε_{11} and ε_{22}) are set to $\varepsilon_{//}$, we obtain ε_{33} = 0.7415 which is applied to determine the degree of strain in the other direction, using the experimental Poisson ratio of 0.27 for the uniaxially strained structures.

3. Results and discussion

3.1. Bulk Ge band structure

The HSE06 approximation relies on error compensation between the HF and PBE exchange for eliminating the electron self-interaction error and the derivative discontinuity. Because it does not use Ge-specific parameters, its accuracy in reproducing the delicate difference between the direct and indirect gap is somewhat limited; nevertheless, the method is expected to encapsulate the basic physics involved with strain-induced changes. However, hybrid functionals are still computationally expensive for large systems.

The computational cost of the DFT+U approach is approximately the same as that of LDA/GGA, and MGGA costs marginally more than standard GGA. This places these methods at a significant advantage for large supercell calculations required to simulate *e.g.*, interfaces for CMOS devices or doping in moderate concentration for optoelectronics.

DFT+U methods include a correction for the on-site Coulomb interactions in addition to the standard exchange–correlation functional. The Hubbard U parameter may be varied simultaneously for various orbitals of the same type of atom, e.g., for the p and d orbitals of Ge. The U parameters can be chosen to best reproduce both the equilibrium lattice constant (as shown in Fig. 1) and the band structures (as shown in Fig. 2). Once these parameters are determined for the bulk phases, the expectation is that they can be used to describe the material properties under external strain and various temperature and pressure conditions. We tested this assumption by comparing the results to those of HSE06 and TB09.