Understanding the Structure of Germanium Sulfide (GeS)

Miguel Castro-Rivera, 2018 PARADIM REU Intern

Mechanical Engineering, Inter-American University of Puerto Rico, Bayamon Campus

REU Program: 2018 Platform for the Accelerated Realization, Analysis and Discovery of Interface Materials Research Experience for Undergraduates (PARADIM REU) Program

PARADIM REU Principal Investigator: Prof. Darrell Schlom, Materials Science and Engineering, Cornell University

PARADIM REU Mentor: Dr. Betül Pamuk, Department of Applied and Engineering Physics, Cornell University

Primary Source of PARADIM REU Funding: Support for PARADIM is provided under NSF Grant # DMR-1539918 as part of the Materials Innovation Platform Program

Contact: mcastro1222@interbayamon.edu, schlom@cornell.edu, betul.pamuk@cornell.edu

Websites: http://paradim.cornell.edu/education, http://www.cnf.cornell.edu/cnf_2018reu.html

Abstract:

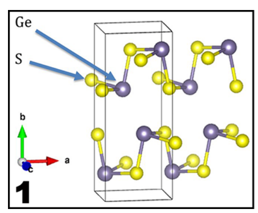
The purpose of this project was to manipulate GeS band gap by applying bi-axial strain to the material with the goal of optimizing the gap. To complete this process, we used computational methods with density functional theory (DFT). We obtained an indirect band gap E_g = 0.78 eV, almost half of the experimental result. When the structure was strained, the gap remained indirect and increased to 0.87 eV for 5% tensile, while for 5% compressive, the gap closed completely. However, an interesting behavior was observed between 0% and 2% tensile, the conduction band minimum (CBM) changed from being at Γ, to a point in between Γ → X path.

Introduction:

Finding an alternative sustainable source of energy has turned into one of the most important quests for humanity. Out of the many different sources, solar power is one that shows a lot of promise. Energy from the sun has the potential of supplying the planet energy demand of 363 terawatt hours per day in a matter of seconds, but this is limited due to the high cost of silicon-based photovoltaics (PVs) and their low conversion efficiency (e.g. ~ 31%) [1]. One key aspect to improving the efficiency of PVs lies in the capture and conversion of the energy obtained from solar photons. Because photons with energy lower to the band gap of the material are not absorbed, and those with higher energy release heat due to electron relaxation through the bands, it is essential that any PV material has a band gap close to the optimal absorption value, e.g. ~ 1.3 eV [2]. A potential substitute for Si-based PVs is GeS, due to its abundance and non-toxic properties [3]. One complication remains, GeS has a ~ 1.74 eV gap [4]. Therefore, using density function theory (DFT), we decided to alter GeS to obtain a more ideal band gap.

Methods:

We used a projector augmented wave pseudopotentials method with an electronic energy convergence of 10^{-8} eV



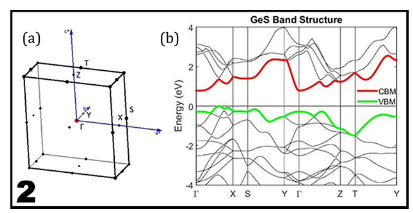


Figure 1, left: Orthorhombic GeS structure. Figure 2, right: (a) BZ path used from [9]. (b) Band results. Conduction band minimum (CBM). Valence band maximum (VBM).

and a force tolerance of 10^{-3} eV/Å [5], which are included in the VASP package [6,7]. We implemented the parametrization scheme of Perdew-Burke-Ernzerhof for solids (PBEsol) with the generalized gradient approximation (GGA) for the exchange and correlation functional within DFT. After loading the structure into VASP, we used a converged value of 650 eV for energy cutoff and an electronic momentum mesh of size 12 × 6 × 12 for the sampling of the Brillouin Zone (BZ). GeS has a layered crystal structure containing eight atoms in the primitive unit cell. The initial parameters used for GeS are from [8]. After relaxing the crystal structure, the ground state parameters were the following: a = 4.14 Å, b = 10.35 Å and c = 3.67 Å. The crystal structure representation of GeS, the band structure and BZ can be seen in Figure 1 and 2 respectively.

Using DFT, we started to strain GeS bi-axially (± 5%, 1% step) by changing and fixing lattice parameters "a" and "c" simultaneously to their respective new values. A visual representation is shown in Figure 3 (a) and (b).

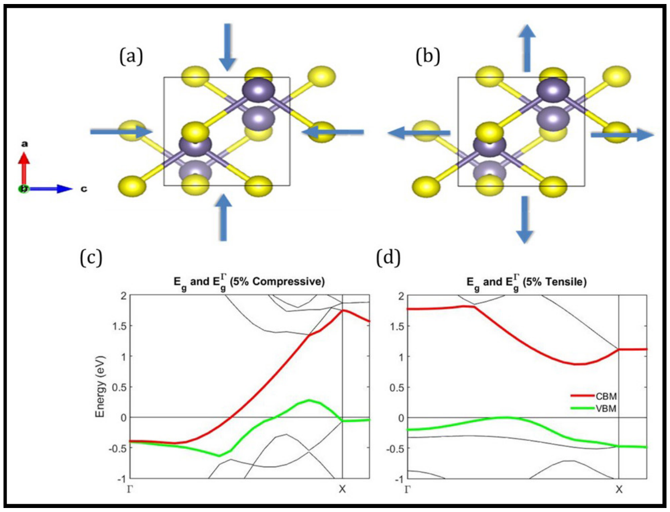


Figure 3: (a) Compressive bi-axial strain. (b) Tensile bi-axial strain. (c) Closing of the gap at 5% compressive strain. (d) E_g *= 0.87 eV and* E_g^Γ *= 1.98 eV at 5% tensile strain.*

Results and Conclusions:

We analyzed the fundamental indirect gap of E_g = 0.78 eV between valence band maximum (VBM) in the Γ → X direction and CBM at Γ. We also observed a direct gap E_g^Γ = 1.06 eV at Γ symmetry point. This was due to how close both gaps are in value, and also because a direct gap has less energy loss than an indirect gap. As it is shown in Figure 3 (c), we found that when we applied 5% compressive strain, both E_g and E_g^Γ became zero because the valence and conduction band intersected one another. When it was 5% tensile strained (Figure 3 (d)), both gaps increased, E_g = 0.87 eV and E_g^Γ = 1.98 eV, unfortunately making E_g^Γ too big to remain a competing gap. Also, Figure 4 shows how E_g and E_g^Γ behaved with different strain values. The unstrained result under-estimated the experimental value of 1.74 eV [4]. This indicates some issues in the approximating methods. However, we observed that with tensile strain, CBM changed from Γ point to a position in between the Γ and X path. This opens the possibility of E_g changing from indirect to a direct gap at some point in between.

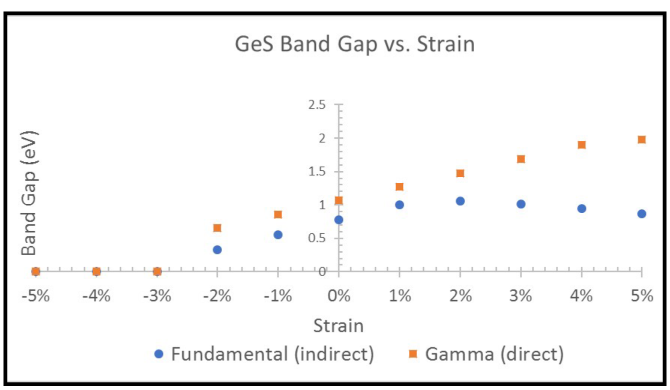


Figure 4: Summary of E_g *and* E_g^Γ *band gap results.*

Future Work:

We will improve the modeling methods to obtain a better match to the experimental gap and decrease the strain step-size to 0.2% around the transition phase between 1% and 2% tensile strain with the hopes of observing a direct gap.

Acknowledgements:

Support for PARADIM is provided under DMR-1539918 as part of the NSF Materials Innovation Platform Program. Calculations performed at Tardis computer cluster at Cornell University Center for Advanced Computing (CAC), with access given by Prof. Fennie. Special thanks to the PARADIM and CNF staff, and my fellow PARADIM interns.

References:

[1] N. S. Lewis, Science 315, 798 (2007).
[2] L. Zhu, T., et. al, Opt. Express 24, A740 (2016).
[3] P. D. Antunez, et. al, Nanoscale 3, 2399 (2011).
[4] D. D. Vaughn, et. al, J. Am. Chem. Soc. 132, 15170 (2010).
[5] J. P. Perdew, et. al, Phys. Rev. Lett. 100, 136406 (2008).
[6] G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
[7] G. Kresse and J. Hafner, Phys. Rev. B 47, 558 (1993).
[8] J. M. Skelton, et. al, J. Phys. Chem. C 121, 6446 (2017).
[9] L. Makinistian and E. A. Albanesi, Phys. Rev. B 74, 045206 (2006).