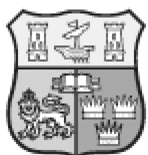
CORA Cork Open Research Archive
Cartlann Taighde Oscailte Chorcaí

UCC Library and UCC researchers have made this item openly available. Please let us know how this has helped you. Thanks!

Title	Hexagonal SixGe1-xas a direct-gap semiconductor
Author(s)	Broderick, Christopher A.
Publication date	2022-08-22
Original citation	Broderick, Christopher A. (2022) 'Hexagonal SixGe1-xas a direct-gap semiconductor', 2022 IEEE Photonics Society Summer Topicals Meeting Series (SUM), Cabo San Lucas, Mexico, 11-13 July. doi: 10.1109/SUM53465.2022.9858220
Type of publication	Conference item
Link to publisher's version	http://dx.doi.org/10.1109/SUM53465.2022.9858220 Access to the full text of the published version may require a subscription.
Rights	**© 2022, IEEE. Personal use of this material is permitted. Permission from IEEE must be obtained for all other uses, in any current or future media, including reprinting/republishing this material for advertising or promotional purposes, creating new collective works, for resale or redistribution to servers or lists, or reuse of any copyrighted component of this work in other works.**
Item downloaded from	http://hdl.handle.net/10468/13774

Downloaded on 2022-12-08T08:29:51Z



UCC
University College Cork, Ireland
Coláiste na hOllscoile Corcaigh

Hexagonal Si_xGe_{1-x} as a direct-gap semiconductor

Christopher A. Broderick[1,2,3,*]
[1]Materials Department, University of California, Santa Barbara, California 93106-5050, U.S.A.
[2]Tyndall National Institute, University College Cork, Lee Maltings, Dyke Parade, Cork T12 R5CP, Ireland
[3]Department of Physics, University College Cork, Cork T12 YN60, Ireland
*Email: c.broderick@umail.ucc.ie

***Abstract*—The band gap of germanium (Ge) is "weakly" indirect, with the L_{6c} conduction band (CB) minimum lying only ≈ 150 meV below the zone-center Γ_{7c} CB edge in energy. This has stimulated significant interest in engineering the band structure of Ge, with the aim of realizing a direct-gap group-IV semiconductor compatible with established complementary metal-oxide-semiconductor fabrication and processing infrastructure. Recent advances in nanowire fabrication now allow growth of Ge in the metastable lonsdaleite ("hexagonal diamond") phase, reproducibly and with high crystalline quality. In its lonsdaleite allotrope Ge is a direct- and narrow-gap semiconductor, in which the zone-center Γ_{8c} CB minimum originates via back-folding of the L_{6c} CB minimum of the conventional cubic (diamond) phase. Here, we analyze the electronic structure evolution in direct-gap lonsdaleite Si_xGe_{1-x} alloys from first principles, using a combination of alloy supercell calculations and zone unfolding. We confirm the Si composition range $x \lesssim 25\%$ across which Si_xGe_{1-x} possesses a direct band gap, quantify the impact of alloy-induced band hybridization on the inter-band optical matrix elements, and describe qualitatively the consequences of the alloy band structure for carrier recombination.**

I. Introduction

Despite their impressive electrical characteristics, the indirect band gaps of silicon (Si) and Ge have impeded the development of efficient active photonic devices – light-emitting diodes and semiconductor lasers – for Si photonics applications. To overcome this persistent issue, several approaches are being pursued to monolithically integrate direct-gap semiconductors on Si substrates. These efforts fall into two broad categories: (i) heterogeneous integration of III-V semiconductors on Si [1], and (ii) band structure engineering of group-IV semiconductors [2]. While the former approach has produced semiconductor lasers with impressive performance, growth of III-V device structures on Si with low defect densities is technically challenging due to mismatches in lattice parameter, thermal expansivity and polarity between group-IV and III-V materials. The latter approach has recently attracted increasing interest, due to demonstrations of direct-gap-like behavior and electrically pumped lasing in tensile-strained Ge, and in $Ge_{1-x}Sn_x$ alloys containing tin (Sn). An emerging approach to this long-standing problem centers on so-called crystal phase engineering: growing conventional Si_xGe_{1-x} alloys in unconventional metastable hexagonal phases, to exploit the resulting modifications to the electronic band structure.

Theoretically, it is well established that the metastable lonsdaleite (hexagonal) phase of Ge is a direct-gap semiconductor, in which the zone-center Γ_{8c} CB minimum originates from back-folding of the L_{6c} CB minimum of the conventional diamond (cubic) phase [3]. Recently, high-quality growth of lonsdaleite Si_xGe_{1-x} has been realized, with the demonstration of room temperature light emission attracting significant attention [4]. This observed light emission is surprising from a theoretical perspective, since the fundamental Γ_{8c}-Γ_{9v} band gap of lonsdaleite Ge is "pseudo-direct", possessing near-vanishing optical matrix elements. Here, we investigate the electronic structure evolution in lonsdaleite Si_xGe_{1-x} from first principles using alloy supercell calculations, and directly interrogate the oscillator strength associated with the direct band gap. Our calculations indicate that the acquisition of Ge Γ_{8c} character by the alloy CB minimum is insufficient to explain measured sub-ns carrier lifetimes, suggesting the potential importance of non-radiative recombination.

II. Theoretical model

Our analysis employs density functional theory (DFT) calculations in the projector augmented-wave (PAW) formalism, implemented using the Vienna Ab-initio Simulation Package (VASP) [5]. Lattice relaxations are performed in the local density approximation (LDA), and electronic structure calculations are performed using the Tran-Blaha modified Becke-Johnson (TB-mBJ) meta-generalized gradient exchange-correlation potential [6]. We perform calculations for 32-atom ($2 \times 2 \times 2$) and 108-atom ($3 \times 3 \times 3$) supercells. We investigate the impact of short-range alloy disorder on the electronic structure via comparative analysis of ordered Si_1Ge_{N-1} ($x = N^{-1}$) and disordered Si_MGe_{N-M} ($x = \frac{M}{N}$) supercells, with alloy disorder in the latter represented using a special quasi-random structure (SQS) approach [7]. We compute alloy supercell effective band structures via zone unfolding [8], using the BandUP code [9]. In the presence of carrier densities corresponding to practical applications, $n \approx p \lesssim 10^{18}$ cm^{-3}, injected electrons and holes occupy states in a small fraction of the Brillouin zone, at and immediately adjacent to the Γ-point. In order to quantify the impact of alloying on the radiative recombination rate we therefore consider in detail the impact of the alloy microstructure on the zone-center inter-band optical matrix elements, computed directly in the PAW formalism.

III. Results

Figures 1(a) and 1(b) compare the crystal structures of conventional (cubic) diamond and metastable (hexagonal) lonsdaleite. The 4-atom primitive unit cell of [0001]-oriented lonsdaleite is closely related to the 6-atom unit cell of [111]-oriented diamond: the latter can be thought of as originating from the former by rotating atoms "5" of Fig. 1(a) clockwise about the [111] axis by 120°. In this manner, metastable lonsdaleite represents a shortening of the unit cell along [111], resulting in back-folding of the Γ-L bands. This is observed by examining our DFT-calculated lonsdaleite Ge band structure in Fig. 1(b): beginning from the Γ_{7c} CB – common to the diamond and lonsdaleite phases – and tracking the dispersion along [0001], we observe band folding at the A-point, giving rise to Γ_{8c} and hence a narrow, direct band gap. Recent

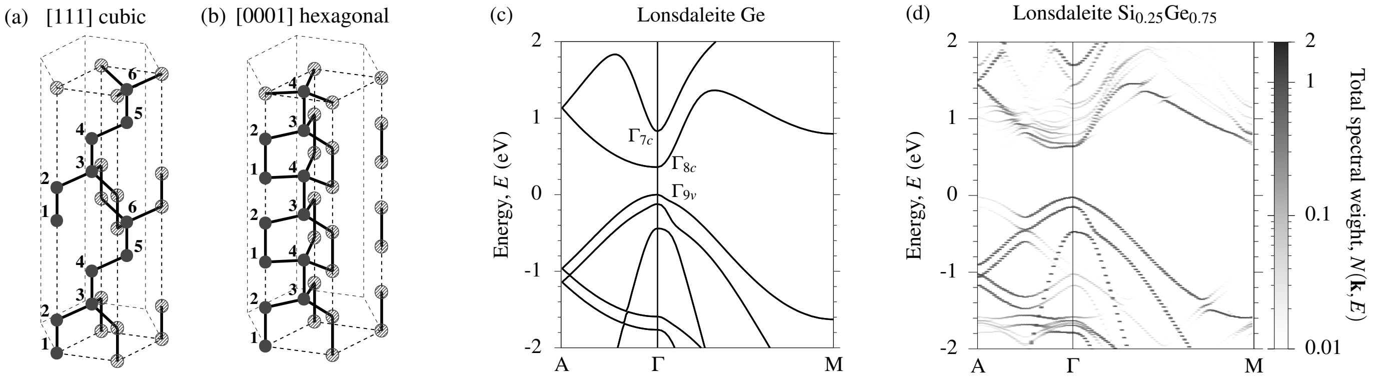


Fig. 1. Illustration of the (a) [111]-oriented diamond, and (b) [0001]-oriented lonsdaleite crystal structures. (c) DFT-calculated band structure of lonsdaleite Ge. (d) Effective band structure of a 32-atom Si_8Ge_{24} ($x = 25\%$) SQS, displaying alloy-induced CB hybridization and the direct- to indirect-gap crossover.

DFT calculations have demonstrated that this Γ_{8c}-Γ_{9v} band gap possesses weak oscillator strength $\lesssim 10^{-2}$ [4], a finding quantitatively corroborated by the present analysis.

Figure 1(d) shows the effective band structure calculated for a disordered, 32-atom lonsdaleite Si_8Ge_{24} ($x = 25\%$) SQS, where the total spectral weight (Bloch character) is plotted on a logarithmic scale to emphasise features indicative of alloy-induced CB hybridization. Indeed, while the alloy band structure close in energy to the valence band maximum remains close to that of lonsdaleite Ge, the near-zone-center CB structure is comparatively strongly perturbed, with "echoes" in the Bloch character being indicative of distinct bulk states that back-fold to the same supercell wave vector hybridizing with one another [10]. We note that this Si composition is at the cusp of the direct- to indirect-gap crossover for the alloy: for higher Si compositions the CB minimum lies at the M-point, as in indirect-gap lonsdaleite Si [3]. Our calculated alloy supercell zone-center inter-band optical matrix elements quantify the impact of (i) alloy-induced CB hybridization, and (ii) the alloy microstructure, on the direct-gap oscillator strength. For the SQS of Fig. 1(d) we compute a sizeable enhancement in oscillator strength, which is increased by approximately one order of magnitude compared to that associated with the Γ_{8c}-Γ_{9v} band gap of pure lonsdaleite Ge. However, this enhanced oscillator strength is still approximately two orders of magnitude smaller than that associated with the zone-center Γ_{7c}-Γ_{8v} band gap of conventional, diamond-structured Ge.

IV. Conclusion

We have analysed the evolution of the electronic and optical properties of Ge-rich lonsdaleite Si_xGe_{1-x} alloys from first principles. Our alloy supercell DFT calculations confirm the presence of a "pseudo-direct" band gap in the Si composition range $x \lesssim 25\%$, beyond which composition the alloy is indirect-gap. Effective band structure calculations indicate that alloy-induced band hybridization strongly impacts the electronic structure close in energy to the CB minimum. Our calculations predict low-temperature direct band gaps ≈ 0.35 – 0.65 eV for $x \lesssim 25\%$, increasing approximately linearly with Si composition. Our analysis suggests that the expected impact of the hybridization-induced enhancement of near-zone-center optical matrix elements on the radiative recombination rate is minimal. Estimates based on these calculations describe radiative lifetimes several orders of magnitude larger than experimentally observed carrier lifetimes. This, combined with the known low defect density and expected absence of mid-gap defect states in experimentally analysed lonsdaleite Si_xGe_{1-x} samples, suggests that non-radiative recombination could play an important role in this emerging material system.

Acknowledgement

This work was supported by the European Union's Horizon 2020 programme for research and innovation via a Marie Skłodowska-Curie Actions Individual Fellowship (H2020-MSCA-IF; project "SATORI", grant agreement no. 101030927).

References

[1] D. Liang and J. E. Bowers, "Recent progress in heterogeneous III-V-on-silicon photonic integration," *Light: Adv. Maunf.*, vol. 2, p. 5, 2021.

[2] R. Geiger, T. Zabel, and H. Sigg, "Group IV direct gap photonics: methods, challenges, and opportunities," *Front. Mater.*, vol. 2, p. 52, 2015.

[3] A. De and C. E. Pryor, "Electronic structure and optical properties of Si, Ge and diamond in the lonsdaleite phase," *J. Phys.: Condens. Matter*, vol. 26, p. 145801, 2014.

[4] E. M. T. Fadaly, A. Dijkstra, J. R. Suckert, D. Ziss, M. A. J. van Tilburg, C. Mao, Y. Ren, V. T. van Lange, K. Korzun, S. Kölling, M. A. Verheijen, D. Busse, C. Rödl, J. Furthmüller, F. Bechstedt, J. Stangl, J. J. Finley, S. Botti, J. E. M. Haverkort, and E. P. A. M. Bakkers, "Direct-bandgap emission from hexagonal Ge and SiGe alloys," *Nature*, vol. 580, p. 205, 2020.

[5] G. Kresse and D. Joubert, "From ultrasoft pseudopotentials to the projector augmented-wave method," *Phys. Rev. B*, vol. 59, p. 1758, 1999.

[6] F. Tran and P. Blaha, "Accurate band gaps of semiconductors and insulators with a semilocal exchange-correlation potential," *Phys. Rev. Lett.*, vol. 226401, p. 102, 2009.

[7] A. Zunger, S.-H. Wei, L. G. Ferreira, and J. E. Bernard, "Special quasirandom structures," *Phys. Rev. Lett.*, vol. 65, p. 353, 1990.

[8] C. A. Broderick, "Electronic structure of lonsdaleite Si_xGe_{1-x} alloys," in *Proc. Int. Conf. Numer. Simul. Optoelectron. Devices (NUSOD)*, 2020.

[9] P. V. C. Medeiros, S. S. Tsirkin, S. Stafström, and J. Björk, "Unfolding spinor wave functions and expectation values of general operators: introducing the unfolding-density operator," *Phys. Rev. B*, vol. 91, p. 041116(R), 2015.

[10] P. M. Pearce, C. A. Broderick, M. P. Neilsen, A. D. Johnson, and N. J. Ekins-Daukes, "Electronic and optical properties of $Si_xGe_{1-x-y}Sn_y$ alloys lattice-matched to Ge," *Phys. Rev. Materials*, vol. 6, p. 015402, 2022.