First-Principles Theory of Optical Emission in Nanostructured Hexagonal Ge

Christopher A. Broderick[1,2,3], Xie Zhang[4], Mark E. Turiansky[1] and Chris G. Van de Walle[1]

[1]*Materials Department, University of California, Santa Barbara, California 93106, U.S.A.*

[2]*Tyndall National Institute, University College Cork, Lee Maltings, Dyke Parade, Cork T12 R5CP, Ireland*

[3]*School of Physics, University College Cork, Cork T12 YN60, Ireland*

[4]*School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, China*

christopher.broderick@ucc.ie

Demonstrations of optical emission from Si_xGe_{1-x} nanowires (NWs) grown in the metastable lonsdaleite (hexagonal, 2H) phase herald the emergence of a new candidate direct-gap group-IV semiconductor for Si photonics [1]. This is driving increased interest in crystal phase engineering: treating the underlying crystal structure of a semiconductor as a novel degree of freedom to engineer its optoelectronic properties. We present a theoretical analysis, based on first-principles calculations, of optical emission from (i) bulk 2H-Ge, and (ii) polytype heterostructures (PHs) formed by alternating between the conventional diamond (cubic, 3C) and 2H phases of Ge.

Using density functional theory (DFT), and employing an adaptive **k**-point grid approach to enable dense sampling of the Brillouin zone [2], we compute spontaneous emission (SE) spectra for bulk-like 2H-Ge. Our calculations accurately capture the evolution of the measured photoluminescence (PL) spectra of Ref. [1], including their dependence on temperature and carrier density. Our calculations corroborate that the experimentally observed PL corresponds to radiative recombination across the direct fundamental band gap. However, computing the radiative recombination coefficient B via the integrated SE indicates that the measured carrier lifetime in initial 2H-Ge NWs is dominated by as-yet unquantified non-radiative recombination processes. We confirm the predicted presence of a pseudo-direct- to direct-gap transition under application of [0001] uniaxial tension [3], and demonstrate that application of [0001] uniaxial tension can enhance B by approximately two orders of magnitude at fixed band gap. This suggests the possibility to realise a radiative recombination rate close to that of a conventional (3C) III-V semiconductor in a strain-engineered direct-gap group-IV material.

Comparing calculated SE spectra vs. carrier density to power-dependent PL measurements, we elucidate the experimentally observed emergence and dominance of a second, higher-energy PL peak with increasing excitation intensity. The separation in energy between these two PL peaks is lower than either the conduction or valence subband splitting, suggesting an unusual situation in which multiple PL peaks emerge with increasing carrier density when the radiative recombination involves only a single subband pair. We elucidate this unusual behavior via the atypical dependence on wave vector **k** of the 2H-Ge optical matrix elements.

We predict trends in the optoelectronic properties of 2H/3C-Ge PHs, which are naturally present in as-grown 2H-Ge NWs due to their incomplete phase purity. We confirm predicted type-I band offsets in 2H/3C-Ge PHs [4], which generate quantum confinement of electrons and holes in 2H-Ge "wells" surrounded by 3C-Ge "barriers". We quantify the tuneability of the band gap across the application-rich 3 – 5 μm wavelength range, and demonstrate that short-period 2H/3C-Ge PHs can enhance the radiative recombination rate by up to an order of magnitude vs. bulk 2H-Ge.

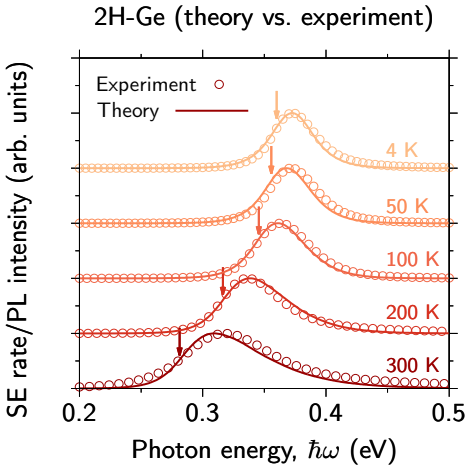

Fig. 1. Calculated SE (solid lines) and measured PL (open circles) spectra for 2H-Ge at temperatures $T = 4$, 50, 100, 200 and 300 K (darkening colors). Arrows denote the fundamental direct band gap. Experimental data are from Ref. [1].

References

[1] E. M. T. Fadaly, A. Dijkstra, J. R. Suckert, D. Ziss, M. A. J. van Tilburg, C. Mao et al., Nature **580**, 205 (2020).

[2] X. Zhang, J.-X. Shen, W. Wang and C. G. Van de Walle, ACS Energy Lett. **3**, 2329 (2018).

[3] J. R. Suckert, C. Rödl, J. Furthmüller, F. Bechstedt and S. Botti, Phys. Rev. Materials **5**, 024602 (2021).

[4] T. Kaewmaraya, L. Vincent and M. Amato, J. Phys. Chem. C **121**, 5820 (2017).