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# Multi-scale theory and simulation of direct-gap group-IV semiconductor alloys

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**Abstract**—Alloying of Ge with other group-IV elements – C, Sn or Pb – represents a promising route to realise direct-gap group-IV semiconductors for applications in Si-compatible devices, including light-emitting diodes and lasers, as well as tunnelling field-effect transistors and multi-junction solar cells. To develop a quantitative understanding of the properties and potential of group-IV alloys, we have established a multi-scale simulation framework to enable predictive analysis of their structural and electronic properties. We provide an overview of these simulation capabilities, and describe previously overlooked fundamental aspects of the electronic structure evolution and indirect- to direct-gap transition in  $(\text{Si})\text{Ge}_{1-x}(\text{C},\text{Sn},\text{Pb})_x$  alloys. We further describe ongoing work related to exploiting this simulation platform to compute the optical and transport properties of  $(\text{Si})\text{Ge}_{1-x}\text{Sn}_x$  alloys and heterostructures.

## I. INTRODUCTION

The group-IV semiconductors Si and Ge underpin contemporary microelectronics, and have been used to develop passive photonic components. However, their indirect band gaps limit applications in active photonic devices such as light-emitting diodes and lasers. Since the fundamental indirect band gap of Ge is only  $\approx 150$  meV lower than its direct band gap, strong interest in engineering a direct band gap by alloying Ge with C, Sn or Pb has developed. While this emerging class of alloys has recently attracted significant and growing attention, there remains a lack of fundamental quantitative knowledge regarding the mechanisms driving the evolution of their electronic structure, and the implications of the alloy electronic structure for proposed applications in photonics (e.g.  $(\text{Si})\text{Ge}_{1-x}\text{Sn}_x$ -based lasers [1]), in electronics (e.g.  $\text{Ge}_{1-x}\text{Sn}_x$ -based tunnelling field-effect transistors [2]), and in photovoltaics (e.g. lattice-matched  $\text{Si}_y\text{Ge}_{1-x-y}\text{Sn}_x/\text{Ge}$  as a 1 eV band gap material for multi-junction solar cells [3]).

To provide fundamental insight into  $(\text{Si})\text{Ge}_{1-x}(\text{C},\text{Sn},\text{Pb})_x$  alloys we have developed a multi-scale approach to enable large-scale, high-throughput atomistic analysis of alloy properties, and to accurately parametrise continuum models for applications in heterostructure calculations. Such capabilities are required to understand the nature of the alloy electronic structure, the consequences of which must be understood to enable quantitative prediction of technologically relevant material properties for targeted applications. Here, we provide an overview of our simulation capabilities for candidate direct-gap group-IV semiconductor alloys, summarise our findings regarding electronic structure evolution due to C, Sn or Pb incorporation in Ge, and describe ongoing atomistic and continuum investigations of the optical and transport properties of  $(\text{Si})\text{Ge}_{1-x}\text{Sn}_x$  alloys and heterostructures.

## II. MULTI-SCALE SIMULATION FRAMEWORK

Our simulation framework encompasses first principles atomistic, and semi-empirical atomistic and continuum models of the structural and electronic properties of  $(\text{Si})\text{Ge}_{1-x}(\text{C},\text{Sn},\text{Pb})_x$  alloys (cf. Fig. 1).

We begin with density functional theory (DFT) calculations of the structural and electronic properties of the constituent materials forming the alloys (e.g. Ge,  $\alpha$ -Sn and zb-GeSn for  $\text{Ge}_{1-x}\text{Sn}_x$  alloys). Parameters extracted from DFT calculations parametrise semi-empirical valence force field (VFF) potentials and tight-binding (TB) Hamiltonians for multinary group-IV alloys [4]. The VFF and TB models – benchmarked directly against DFT calculations for alloy supercells containing  $\sim 10^2$  atoms [4] – respectively enable atomistic structural relaxation and electronic structure calculations to be performed for alloy systems containing  $\gtrsim 10^5$  atoms. Applying the TB method to VFF-relaxed supercells provides single-particle eigenstates which serve as a starting point to compute the properties of real alloys. In the first instance, this allows for detailed quantitative analysis of the electronic structure evolution in realistic (large-scale, disordered) alloy structures.

Based on DFT and TB electronic structure calculations we extract composition-dependent band offsets and parametrise continuum multi-band  $\mathbf{k}\cdot\mathbf{p}$  Hamiltonians for group-IV alloys. The availability of accurately parametrised multi-band  $\mathbf{k}\cdot\mathbf{p}$  models allows for quantitative analysis of key properties in quantum-confined heterostructures, enabling in silico design and optimisation of Si-compatible light-emitting devices.

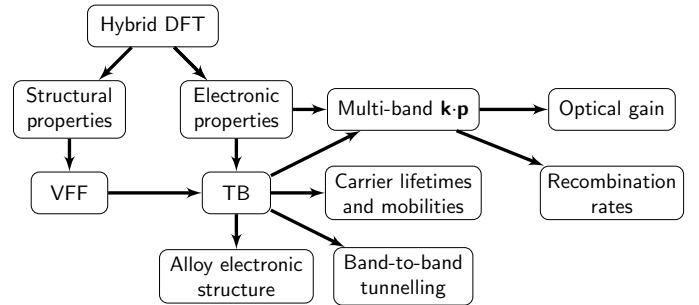


Fig. 1. Schematic illustration of the multi-scale simulation framework for  $(\text{Si})\text{Ge}_{1-x}(\text{C},\text{Sn},\text{Pb})_x$  group-IV alloys described in Sec. II. DFT calculations are used to parametrise atomistic VFF potentials and TB Hamiltonians, allowing to perform large-scale, high-throughput electronic structure calculations. This provides input for atomistic calculations of optical and transport properties, and parameters for continuum multi-band  $\mathbf{k}\cdot\mathbf{p}$  Hamiltonians to facilitate analysis of optical gain and carrier recombination rates in heterostructures.

### III. RESULTS

#### A. Electronic structure evolution

We have analysed the mechanisms driving the indirect-to direct-gap transition in  $\text{Ge}_{1-x}(\text{C}, \text{Sn}, \text{Pb})_x$  alloys, and have quantified the nature of the resultant alloy band edge states.

For  $\text{Ge}_{1-x}\text{Sn}_x$  we highlight the presence of previously unexplored band hybridisation, which significantly modifies the nature of the alloy electronic structure in the composition range ( $x \approx 6\%$ ) of interest for applications in light-emitting diodes and lasers. We demonstrate that Sn incorporation in Ge drives strong mixing of the Ge L- and  $\Gamma$ -point conduction band edge states, leading to hybridised alloy conduction band edge states which are neither purely direct nor indirect in character [4]. This results in an indirect- to direct-gap transition that proceeds continuously with increasing Sn composition  $x$  [5], in contrast to the general assumption in the literature of this transition occurring at a single, critical Sn composition.

For  $\text{Ge}_{1-x}\text{Pb}_x$  we find qualitatively similar electronic structure evolution to  $\text{Ge}_{1-x}\text{Sn}_x$ , but demonstrate quantitatively that band mixing effects are less pronounced than in  $\text{Ge}_{1-x}\text{Sn}_x$ . We predict an extremely rapid direct band gap reduction with increasing Pb composition – by  $\approx 100$  meV per % Pb replacing Ge – and that the alloy undergoes a relatively abrupt indirect- to direct-gap transition for Pb compositions  $x = 3 - 4\%$ . In this composition range we calculate low temperature alloy band gaps  $\approx 0.3$  eV, making direct-gap  $\text{Ge}_{1-x}\text{Pb}_x$  alloys a candidate material system for photonics applications at mid-infrared wavelengths [6].

For dilute  $\text{Ge}_{1-x}\text{C}_x$  we demonstrate, contrary to recent claims, that C incorporation does *not* drive the formation of a direct *optical* band gap. We show that C incorporation facilitates weak hybridisation of the conduction band edge states of the Ge host matrix, leading to the formation of a “quasi-direct” band gap formed primarily of a linear combination of Ge L-point conduction band edge states [7]. Large-scale alloy supercell calculations reveal the formation of a distribution of C-related localised states in disordered  $\text{Ge}_{1-x}\text{C}_x$  alloys, lying energetically within the Ge band gap [8]. We highlight qualitative similarities to the electronic structure of the dilute nitride alloy  $\text{GaN}_x\text{P}_{1-x}$ , and quantitatively rule out dilute  $\text{Ge}_{1-x}\text{C}_x$  alloys as a potential Si-compatible direct-gap semiconductor.

#### B. Optical and transport properties

Building on our electronic structure calculations, we are investigating the consequences of the alloy electronic structure for key material properties in  $(\text{Si})\text{Ge}_{1-x}\text{Sn}_x$ . Firstly, large-scale TB calculations of optical and alloy scattering matrix elements respectively provide input to calculations of radiative lifetimes and carrier mobilities. Applying our TB models in full quantum kinetic calculations allows accurate prediction of direct band-to-band tunnelling currents in realistic, disordered bulk and nanowire structures. These atomistic calculations provide vital quantitative predictions of properties relevant to proposed applications in light-emitting devices, tunnelling field-effect transistors and multi-junction solar cells. Secondly, continuum  $\mathbf{k}\cdot\mathbf{p}$  calculations allow to compute optical gain and carrier recombination rates in heterostructures having mid-infrared band gaps. It is well known that nonradiative Auger re-

combination dominates the performance of mid-infrared light-emitters: we report detailed analysis of Auger recombination rates in  $(\text{Si})\text{Ge}_{1-x}\text{Sn}_x$  quantum wells, which we compare to equivalent analysis performed for III-V heterostructures operating at similar wavelengths.

### IV. CONCLUSION

We have established a multi-scale simulation framework for group-IV alloys, providing a suitable basis for predictive analysis of candidate direct-gap alloys and heterostructures for applications in Si-compatible devices. Detailed analysis of electronic structure evolution (i) reaffirms the potential of  $\text{Ge}_{1-x}\text{Sn}_x$  as a Si-compatible direct-gap semiconductor, and offers new fundamental insight regarding the nature of the alloy electronic structure having significant implications for device applications, (ii) identifies  $\text{Ge}_{1-x}\text{Pb}_x$  as a potential Si-compatible direct-gap semiconductor, suitable for mid-infrared applications, and (iii) demonstrates quantitatively that a direct optical band gap does not emerge in dilute  $\text{Ge}_{1-x}\text{C}_x$ . Ongoing analysis focuses on quantifying the consequences of the alloy electronic structure for key material properties relevant to proposed device applications. This includes alloy scattering, carrier mobility and band-to-band tunnelling for applications in electronics, as well as optical gain and carrier recombination rates for applications in photonics and photovoltaics.

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