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Electronic structure of lonsdaleite Si_xGe_{1-x} alloys

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***Abstract*—Conventional diamond-structured silicon (Si) and germanium (Ge) possess indirect fundamental band gaps, limiting their potential for applications in light-emitting devices. However, Si_xGe_{1-x} alloys grown in the lonsdaleite ("hexagonal diamond") phase have recently emerged as a promising direct-gap, Si-compatible material system, with experimental measurements demonstrating strong room temperature photoluminescence. When grown in the lonsdaleite phase, Ge possesses a narrow ($\sim$ 0.3 eV) "pseudo-direct" fundamental band gap. Lonsdaleite Si is indirect-gap ($\sim$ 0.8 eV), creating the possibility to achieve direct-gap lonsdaleite Si_xGe_{1-x} alloys across a Ge-rich composition range. We present a first principles analysis of the electronic and optical properties of lonsdaleite Si_xGe_{1-x} alloys, elucidate the electronic structure evolution and direct- to indirect-gap transition, and describe the impact of alloy band mixing effects on inter-band optical transition strengths.**

I. Introduction

The indirect fundamental band gaps of conventional, diamond-structured Ge and Si make them inefficient light emitters, limiting their potential for applications in active photonic devices such as light-emitting diodes and diode lasers. As a result, realising Si-compatible direct-gap semiconductors – to provide a suitable platform for the development of efficient light emitters for Si photonics applications – has attracted attention for several decades. While significant progress has been made via monolithic integration of III-V diode lasers on Si substrates, this approach presents significant challenges from the perspectives of epitaxy and device thermal management. As such, in recent years there has been a surge of interest in approaches to achieve direct-gap group-IV semiconductors via band structure engineering. The majority of these efforts have focused on applying strain to Ge, or on alloying Ge with tin (Sn) to form the $Ge_{1-x}Sn_x$ alloy, with the intention in both cases being to reduce the energy of the zone-centre Γ_{7c} conduction band (CB) edge states below that of the L_{6c} CB minimum [1]. Alternatively, advancements in materials growth now allow Ge and Si nanowires to be fabricated in the lonsdaleite crystal phase, reproducibly and with high crystalline quality [2]. Indeed, recent experimental measurements have demonstrated impressive optical properties in lonsdaleite Si_xGe_{1-x} alloy nanowires [3], distinguishing group-IV lonsdaleite semiconductors as a promising platform for the development of Si-compatible photonic devices.

From a theoretical perspective, it has long been known that lonsdaleite Ge (2H-Ge) and Si (2H-Si) are respectively direct- and indirect-gap semiconductors. This suggests the possiblity to achieve efficient radiative recombination and a tunable band gap, across the (Ge-rich) composition range within which 2H-Si_xGe_{1-x} possesses a direct band gap. The origin of the direct fundamental band gap of 2H-Ge via back-folding of the L_{6c} CB edge states of diamond-structured Ge is well understood, but accurate prediction of the magnitude of the 2H-Ge and 2H-Si band gaps has only recently become possible with the advent of sufficiently advanced first principles electronic structure methods [4]. However, given the "pseudo-direct" [5] nature of the 2H-Ge fundamental band gap, the origin of the observed high radiative recombination rates in 2H-Si_xGe_{1-x} alloy nanowires has not yet been quantitatively understood. Motivated by this question, we present a first principles analysis of the evolution of the electronic and optical properties, and direct- to indirect-gap transition, in 2H-Si_xGe_{1-x} alloys.

II. Theoretical model

Our analysis of the electronic and optical properties of lonsdaleite Si_xGe_{1-x} alloys is based on density functional theory (DFT). Structural relaxation is performed using both Heyd-Scuseria-Ernzerhof hybrid functional [6] (HSEsol) and local density approximation (LDA) exchange-correlation (XC) functionals, to determine the lattice parameters a and c, and internal parameter u, in *real* 2H-Ge and 2H-Si. Based on an approach we have used to analyse the indirect- to direct-gap transition in diamond-structured $Ge_{1-x}Sn_x$ alloys [7], we utilise HSEsol and Tran-Blaha modified Becke-Johnson [8] (TB-mBJ) XC functionals – using, respectively, HSEsol- and LDA-calculated structural properties – to compute the band structure, band edge deformation potentials and optical matrix elements in 2H-Ge and 2H-Si. Comparison between HSEsol- and TB-mBJ-calculated electronic and optical properties verifies the reliability of the TB-mBJ XC functional: due to its lower computational cost, we apply the latter in our alloy supercell calculations. We investigate the evolution of the electronic and optical properties of 2H-Si_xGe_{1-x} across the full composition range $0 \leq x \leq 1$ using a special quasi-random structure (SQS) approach. We apply zone unfolding to obtain effective alloy band structures, and compute the supercell zone centre optical matrix elements to quantify the impact of alloy band mixing effects on the inter-band optical transition strengths. All DFT calculations were performed using the projector augmented-wave method, as implemented in the Vienna Ab-initio Simulation Package [9] (VASP).

III. Results

Our electronic structure calculations verify the presence of a direct band gap in 2H-Ge [4], and an indirect band gap in 2H-Si [10]. Since the lonsdaleite phase is tetragonal, in both cases the valence band (VB) edge lies at the zone centre. The CB minimum in 2H-Si lies at the M point in the Brillouin zone. We calculate a direct fundamental band gap of 0.319 eV for *real* 2H-Ge. The calculated optical matrix elements between the Γ_{9v} and Γ_{8c} VB and CB edge states in 2H-Ge, combined with symmetry analysis of the associated wave functions, affirms that 2H-Ge admits a pseudo-direct band gap: despite strong spatial overlap between Γ_{9v} and Γ_{8c} wave

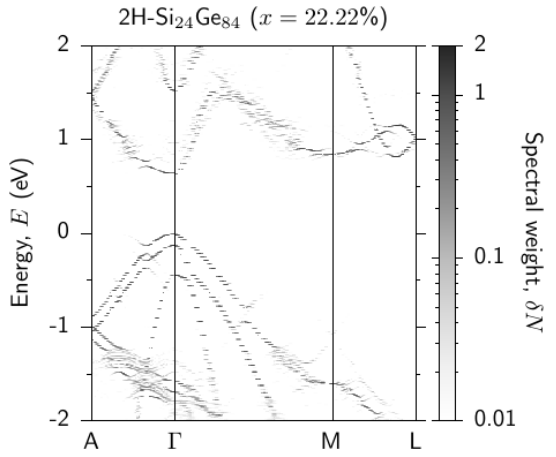

Fig. 1. Effective (unfolded) alloy band structure of a 108-atom lonsdaleite $Si_{24}Ge_{84}$ ($x = 22.22\%$) alloy SQS, demonstrating a direct fundamental band gap. Spectral weight (Bloch character) is indicated by colour, which varies between 0 (white) and 2 (black) for a single, spin-degenerate state.

functions, the optical matrix elements between these states are strongly suppressed (but not forbidden) by symmetry [4].

To analyse the direct- to indirect-gap transition with increasing Si composition x in 2H-Si_xGe_{1-x} alloys, we employ a series of 108-atom ($3 \times 3 \times 3$) SQSs. The atomic positions in each SQS are relaxed via minimisation of the total (free) lattice energy using the LDA XC functional, and band structure of the relaxed SQS is then calculated using the TB-mBJ XC functional. The supercell band structure is then unfolded onto a Brillouin zone associated with a lonsdaleite primitive unit cell defined by the relaxed alloy lattice parameters $a(x)$ and $c(x)$. Figure 1 shows an exemplar alloy effective band structure computed following this approach, for a 2H-$Si_{24}Ge_{84}$ ($x = 22.22\%$) SQS, with x approaching the direct- to indirect-gap transition. We note that the spectral weight (Bloch character) in Fig. 1(c) is displayed on a logarithmic scale, to emphasise the impact of alloy band mixing effects. Indeed, we find that alloy band mixing effects strongly reduce the Bloch character associated with individual states. This effect is most pronounced close in energy to the alloy CB edge, demonstrating that alloy band mixing most strongly perturbs the CB structure. We observe comparatively weak perturbation of the band structure close in energy to the VB edge, reflecting the lack of states – located at points in the Brillouin zone away from the zone centre – which lie sufficiently close in energy to the VB edge to undergo strong band mixing with the zone-centre VB edge states. Our calculated effective alloy band structures suggest that the direct- to indirect-gap transition in 2H-Si_xGe_{1-x} occurs for $x \approx 30\%$, with the CB edge located at the M point in the Brillouin zone for $x \gtrsim 30\%$.

Given the weak optical transition strength associated with the fundamental Γ_{8c}-Γ_{9v} band gap in 2H-Ge [4], recent experimental reports [3] of strong radiative recombination in 2H-Si_xGe_{1-x} are surprising. The authors of Ref. [3] have suggested that this favourable behaviour may originate from enhancement of the optical transition strength associated with the fundamental alloy band gap by alloy mixing effects. To investigate this, we have computed the zone-centre optical matrix elements for inter-band transitions in the 108-atom 2H-Si_xGe_{1-x} SQSs, across the full composition range.

IV. Conclusion

We have undertaken a theoretical analysis of the evolution of the electronic and optical properties with Si composition x in lonsdaleite-structured Si_xGe_{1-x} alloys. Our DFT band structure calculations confirm the presence of a direct fundamental band gap in 2H-Ge, and DFT-calculated optical matrix elements affirm that this band gap is pseudo-direct in nature, having allowed but weak optical transition strength. Effective (unfolded) band structures calculated for 2H-Si_xGe_{1-x} SQSs reveal the presence of strong band mixing effects, which primarily impact the band structure close in energy to the CB edge. The calculated inter-band optical transition strengths emphasise the important role played by band mixing effects in determining the alloy optical properties. Overall, our analysis confirms the potential of lonsdaleite Si_xGe_{1-x} as a Si-compatible, direct-gap semiconductor material system, which is promising for applications in active photonic devices. We conclude that further theoretical analysis is now required to quantify the nature and impact of band mixing effects on properties of 2H-Si_xGe_{1-x} alloys relevant to device applications.

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