Supporting Information: Countinuous-wave magneto-optical determination of the carrier lifetime in coherent $Ge_{1-x}Sn_x$/Ge heterostructures

Elisa Vitiello,[1,*] Simone Rossi,[1] Christopher A. Broderick,[2,3] Giorgio Gravina,[1] Andrea Balocchi,[4] Xavier Marie,[4] Eoin P. O'Reilly,[2,3] Maksym Myronov,[5] and Fabio Pezzoli[1]

[1] *LNESS and Dipartimento di Scienza dei Materiali, Università degli Studi di Milano-Bicocca, via R. Cozzi 55, I-20125 Milano, Italy*
[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*
[4] *Université de Toulouse, INSA-CNRS-UPS, LPCNO, 135 Avenue de Rangueil, 31077 Toulouse, France*
[5] *Department of Physics, The University of Warwick, Coventry CV4 7AL, United Kingdom*

I. THEORETICAL MODEL

A. Model Hamiltonian

The radiative lifetime in an indirect-gap semiconductor is longer than that in a direct-gap material, because indirect radiative recombination involves simultaneous phonon emission or absorption in order to conserve crystal momentum as well as energy. Recent theoretical calculations, [1] supported by pressure-dependent spectroscopic measurements, [2] have shown that the emergence of a direct band gap in $Ge_{1-x}Sn_x$ is characterised by alloy band mixing effects. These calculations and measurements suggest that the $Ge_{1-x}Sn_x$ band gap is formed via hybridisation of the L_{6c} and Γ_{7c} conduction band (CB) edge states of Ge, and that the indirect- to direct-gap transition proceeds continuously with increasing Sn composition x, as the alloy CB edge acquires increasing Γ character. This mixing of partial Γ character into the CB edge states then provides a direct ($\Delta\mathbf{k} = 0$, phonon-free) optical recombination path in a state originating from the Ge L-point CB minimum. We describe here a simple model that can provide a lower limit for the optical recombination lifetime at low Sn composition $x \lesssim 10\%$.

In atomistic electronic structure calculations for ordered N-atom $Ge_{N-1}Sn_1$ supercells, it can be shown [3] that the $Ge_{1-x}Sn_x$ alloy conduction band (CB) edge consists primarily of an admixture of two Ge states: (i) a linear combination $|L_{6c}(A_1)\rangle$ of Ge L_{6c} CB edge states having A_1 symmetry (i.e. purely s-like orbital character) at the substitutional Sn lattice site, and (ii) the zone-centre Ge CB edge state $|\Gamma_{7c}\rangle$. Calculations for ordered supercells provide an upper limit on the extent of this Γ-L band mixing and therefore on the degree of direct-gap (i.e. Ge Γ) character acquired by the $Ge_{1-x}Sn_x$ CB edge at low x. Using a semi-empirical tight-binding (TB) model – parametrised based on density functional theory (DFT) calculations and carefully benchmarked against full DFT alloy supercell electronic structure calculations [1] – we can explicitly construct the basis state $|L_{6c}(A_1)\rangle$ in a given Ge_N supercell. Combining this with the computed Ge Γ_{7c} state, we can use TB alloy supercell calculations to directly parametrise a simple 2-band Hamiltonian which quantitatively describes the hybridised CB edge state obtained from ordered alloy supercell calculations:

$$H(x) = \begin{pmatrix} E(\Gamma_{7c}) - \alpha x & \beta x \\ \beta x & E(L_{6c}) + \gamma x \end{pmatrix} \begin{matrix} |\Gamma_{7c}\rangle \\ |L_{6c}(A_1)\rangle \end{matrix}, \tag{1}$$

where the parameter β describes the strength of the Sn-induced hybridisation between the Ge CB edge states $|\Gamma_{7c}\rangle$ and $|L_{6c}(A_1)\rangle$, which have respective low-temperature energies $E(\Gamma_{7c}) = 0.909$ eV and $E(L_{6c}) = 0.760$ eV relative to the valence band (VB) edge, and α and γ respectively describe Sn-induced "virtual crystal" shifts to the energies of the Γ- and L-point Ge CB basis states. Using ordered supercell TB calculations we compute $\alpha = 2.045$ eV, $\beta = 2.692$ eV, and $\gamma = 2.528$ eV.

Diagonalising Eq. (1), we can compute the Ge Γ_{7c} (direct) character $f_\Gamma(x)$ associated with the alloy CB edge at Sn composition x as

*Electronic address: elisa.vitiello@unimib.it

$$f_\Gamma(x) = \frac{\beta^2 x^2}{\left(E(\Gamma_{7c}) - \alpha x - E_-(x)\right)^2 + \beta^2 x^2}\,, \tag{2}$$

where $E_-(x)$ is the lower energy eigenvalue of Eq. (1) (i.e. the energy of the alloy CB edge).

Our ordered supercell TB calculations reveal that the $Ge_{1-x}Sn_x$ VB edge states remain Ge-like (i.e. retain predominantly Ge Γ_{8v} character) in the Sn composition range of interest here ($x \lesssim 10\%$), and that the VB edge energy displays large bowing. Taking the zero of energy at the Ge VB edge, we compute $E_{\rm VB}(x) = \delta x - b_{\rm VB} x^2$ with $\delta = 1.613$ eV and bowing parameter $b_{\rm VB} = 7.175$ eV.

This information is sufficient to compute the evolution of the character of the alloy band gap, as well as the inter-band optical transition strength associated with radiative recombination involving the hybridised CB edge and Ge-like VB edge states. In what follows, we use this simple model to estimate the Sn composition dependent lifetime $\tau_{\rm R}(x)$ associated with direct radiative recombination in $Ge_{1-x}Sn_x$ at low x.

B. Estimation of radiative lifetime

The lifetime associated with a direct radiative transition is given by [4]

$$\tau_{\rm R} = \frac{2\pi\epsilon_0 m_0 c^3 \hbar^2}{e^2 n_r E_g E_P}\,, \tag{3}$$

where E_g is the band gap, E_P is the Kane parameter describing the inter-band optical transition strength, and n_r is the refractive index.

For radiative recombination involving Ge L-point CB edge and Γ-point VB edge states the transition strength, and hence E_P in Eq. (3), is zero due to the required change in wave vector. In $Ge_{1-x}Sn_x$, the acquisition by the CB edge state of direct Ge Γ character opens a pathway for direct radiative recombination at low x, even when the alloy retains predominantly indirect-gap character. The corresponding direct-gap transition strength varies in the simple model of Sec. I A as $E_P(x) = f_\Gamma(x) E_P(0)$, where $E_P(0)$ is the Kane parameter associated with the direct Γ-point band gap of Ge. Assuming that the change in n_r can be neglected in the Sn composition range considered, we use Eq. (3) to estimate the radiative lifetime $\tau_{\rm R}(x)$ at Sn composition x relative to the lifetime $\tau_{\rm R}(0)$ associated with the direct band gap of Ge

$$\frac{\tau_{\rm R}(x)}{\tau_{\rm R}(0)} = \frac{E_g(0)}{E_g(x) f_\Gamma(x)}\,, \tag{4}$$

where $E_g(0) = E(\Gamma_{7c})$ and $E_g(x) = E_-(x) - E_{\rm VB}(x)$ are respectively the direct band gap of the Ge host matrix semiconductor and the $Ge_{1-x}Sn_x$ alloy band gap.

To obtain an estimate for $\tau_{\rm R}(x)$ using Eq. (4) we require the radiative lifetime $\tau_{\rm R}(0)$ associated with the direct band gap of Ge. We obtain this using the TB model of Ref. 1, which we apply to compute the zone-centre direct-gap radiative recombination rate $\tau_{\rm R}^{-1}(0)$ following Ref. 5. This calculation yields $\tau_{\rm R}(0) = 7.72$ ns, in good quantitative agreement with the value of 8 ns obtained via an equivalent DFT calculation. [5]

C. Discussion

In this simple model $f_\Gamma(0) = 0$, so that evaluation of Eq. (4) for Ge gives $\tau_{\rm R}(x \to 0) \to \infty$. This reflects that the CB edge in Ge is purely L-like, and that an electron occupying an L-valley CB edge state cannot undergo direct radiative recombination with a hole occupying a Γ-point VB edge state. The evolution of $\tau_{\rm R}(x)$ described by Eq. (4) is determined by the product of the alloy band gap $E_g(x)$ and CB edge Γ character $f_\Gamma(x)$, which respectively decrease and increase with increasing x. As x increases the calculated $\tau_{\rm R}(x)$ initially reduces monotonically, reflecting that the alloy CB edge quickly acquires increasing Ge Γ character (cf. Eq. (2)). We compute a minimum value $\tau_{\rm R}(x) \approx 19.1$ ns for $x = 5\%$. We expect Eq. (4) to provide a reliable lower estimate of $\tau_{\rm R}$ at least up to $x = 5\%$, becoming less reliable at larger x, where the 2-band model of Eq. (1) underestimates $f_\Gamma(x)$ compared to that inferred from measured band gap pressure coefficients, [2] and also where the change in n_r with respect to Ge cannot be neglected. With these caveats, we calculate for $x > 5\%$ that the evolution of $\tau_{\rm R}(x)$ described by Eq. (4) is dominated by the reduction in

alloy band gap. Up to $x = 10\%$ we compute that $\tau_{\rm R}(x)$ remains approximately constant at 20 ns, a value which is greater than twice that associated with the direct-gap radiative recombination in Ge (cf. Sec. I B), and an order of magnitude larger than the effective carrier lifetime extracted from our magneto-optical measurements (cf. main text). Recalling from the main text that the extracted effective carrier lifetime τ consists of radiative and non-radiative contributions, $\tau^{-1} = \tau_{\rm R}^{-1} + \tau_{\rm NR}^{-1}$, we can use the above estimate $\tau_{\rm R} \approx 20$ ns to conclude that the effective carrier lifetime extracted from our experimental measurements is dominated by the non-radiative contribution in the whole composition range explored in this work.

We emphasise that the above estimate of $\tau_{\rm R}(x)$ relies on a model of Sn-induced Γ-L CB mixing which is derived explicitly from *ordered* supercell calculations. This simple analysis then neglects the impact of the loss of short-range order associated with substitutional Sn alloy disorder, which we have demonstrated in theoretical calculations to impact the Γ character of the CB edge. [1] In a real, disordered $Ge_{1-x}Sn_x$ alloy, Ge Γ character will be spread across a multiplicity of states lying close in energy to the CB edge, with the details of the CB hybridisation determined by the precise nature of the short- and long-range disorder present in the alloy (leading to inhomogeneous spectral broadening of band edge optical transitions). Nonetheless, high-throughput analysis of the evolution of the CB edge Γ character with Sn composition in large-scale, disordered supercell calculations reveals a qualitatively similar trend to that revealed by Eq. (2): between $x = 0$ and 10%, the Ge Γ character associated with the alloy CB edge states increases monotonically with increasing x. In the context of the present analysis, we therefore expect that more rigorous calculation of $\tau_{\rm R}(x)$ based on atomistic alloy supercell calculations will not significantly modify the trends identified here.

Overall, we conclude that while this simple model estimation can not be expected to produce quantitatively accurate predictions of alloy radiative lifetimes, it should be sufficiently accurate to support our analysis to identify the mechanism(s) dominating effective carrier lifetime. On this basis, our theoretical estimates support the interpretation of our experimental measurements: non-radiative processes having associated lifetimes $\tau_{\rm NR} \approx 1 - 2$ ns dominate the carrier kinetics in the series of $Ge_{1-x}Sn_x$ epitaxial layers investigated in this work.

II. DISLOCATION DENSITY

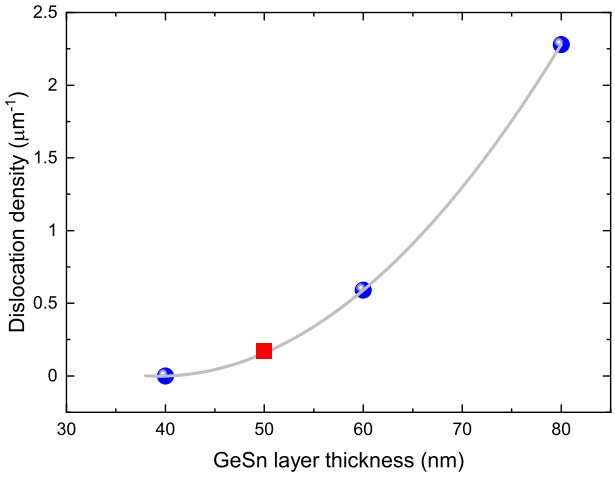

FIG. 1: Dislocation density as a function of the $Ge_{0.92}Sn_{0.08}$ layer thickness. The TEM-measured values (blue dots) increase quadratically with thickness, as depicted by the parabolic fit (grey line). The dislocation density of the 50nm-thick $Ge_{0.92}Sn_{0.08}$ layer was estimated from fit to be about 0.2 μm^{-1} (red square).

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