The nature of the band gap of GeSn alloys

Stefan Schulz[1], Christopher A. Broderick[1,2], Edmond J. O'Halloran[1,3] and Eoin P. O'Reilly[1,2]
[1]Tyndall National Institute, University College Cork, Cork T12 R5CP, Ireland
[2]Department of Physics, University College Cork, Cork, Ireland
[3]Department of Chemistry, University College Cork, Cork, Ireland
Email: stefan.schulz@tyndall.ie

***Abstract*—We present a detailed analysis of the electronic structure of GeSn alloys using density functional theory. Special attention is paid to Sn-induced conduction band mixing effects. Our calculations indicate a continuous evolution from an indirect to a direct band gap material with increasing Sn content. This finding is in stark contrast to the literature perception of a sharp transition at a fixed critical Sn composition. Finally, we discuss and present initial results on how the density functional data is used to establish semi-empirical tight-binding models.**

***Index Terms*—GeSn alloys, electronic structure**

I. Introduction

Germanium-tin (GeSn) alloys have attracted considerable interest due to their potential for next-generation optoelectronic devices, given that GeSn presents the first tunable group-IV semiconductor alloy that allows for a direct band gap material while still being compatible with silicon (Si) [1], [2]. Research activities surrounding GeSn have thus gathered enormous pace.

Of central importance for applying GeSn alloys in future optoelectronic devices is a detailed understanding of how the nature of the band gap changes with Sn composition. Ge is intrinsically an *indirect* band gap material; the lowest conduction band (CB) state at the Γ-point is approximately 140 meV above the CB L-states [3]. The widely made assumption about the evolution of the GeSn band gap is that with increasing Sn content, the CB state at Γ is lowered until it is energetically below the CB minimum L-states. Using this picture, a critical Sn content is expected at which a *sharp* transition from an indirect to a direct band gap material occurs. Basically all previous theoretical and experimental studies rely on this concept [2], [4]. However, this approach completely neglects Sn induced band mixing effects between Γ- and L-CB states. In fact, in theoretical studies, supercells (SCs) have been chosen to avoid this mixing [4]. In general, for an alloy with strong band mixing effects, it is more appropriate to discuss the fractional Γ-character of the lowest CB state, rather classifying it as being an indirect or direct gap material. For optical properties the fractional Γ character is of central importance [5]. In this work, using hybrid functional density functional theory (HSE-DFT) and taking CB state mixing effects into account, we find that the evolution of the nature of the GeSn band gap is continuous, in contrast to the widely accepted idea of a sharp indirect-to-direct gap transition [7]. Our theoretical findings are in good agreement with experimental studies [6], [7]. Also, we present initial results on how the HSE-DFT data can be used to establish accurate tight-binding (TB) models, offering the opportunity to study large SCs and thus to address the impact of the alloy microstructure on the band gap evolution across the full experimentally relevant Sn composition range.

II. Theoretical Framework

To study the electronic structure of GeSn alloys, we use density functional theory (DFT) within the (improved) Heyd Scuseria Ernzerhof (HSE) hybrid functional scheme for solids (HSEsol) [8]. This approach circumvents the band gap problem of standard (e.g. LDA) DFT. The exact exchange mixing parameter is 0.3, spin-orbit coupling is included, the plane wave cut-off energy is 400 eV and a $6 \times 6 \times 6$ k-point mesh has been chosen for bulk calculations. The here relevant bulk band structure features (e.g. CB $\Gamma - L$ state separation) of Ge and α-Sn are accurately described. For instance, the calculated energetic separation between the lowest CB states at Γ and L in Ge is 143 meV, thus in excellent agreement with the experimental value of 140 meV [3]. All calculations have been carried out using the DFT package VASP [9].

III. Results

To gain insight into potential CB mixing effects in GeSn alloys and how the CB structure evolves with Sn content, we proceed in the following way. First, SCs where the CB L-states of the primitive cell fold back to the Γ-point of the SC have been chosen. To achieve this, we have considered cubic 64 atom SCs. We have studied here two systems. The first one is one with a very low Sn content (1.56%). In this case 1 of the 64 Ge atoms has been replaced by a Sn atom. The second structure uses a 64 Ge SC where 4 Ge atoms have been replaced by 4 Sn atoms (6.25% Sn) at randomly chosen lattice sites. It should be noted that in the literature a wide range of Sn content thresholds (6-11% Sn) have been reported at which the sharp indirect-to-direct band gap transition occurs [2]. Thus, the here analyzed Sn contents are either well below (1.56% Sn) or at the edge (6.25% Sn) of this threshold.

To investigate the nature of the band gap in GeSn alloys, we have performed pressure dependent electronic structure calculations for the different GeSn SCs. If there is a sharp transition from an indirect to a direct gap material, the pressure coefficient of the alloy band gap should follow either the pressure coefficient of the fundamental Ge indirect gap or the value of the Ge direct gap at Γ. Figure 1 depicts the (DFT) calculated variation of band gap with applied pressure (filled symbols).

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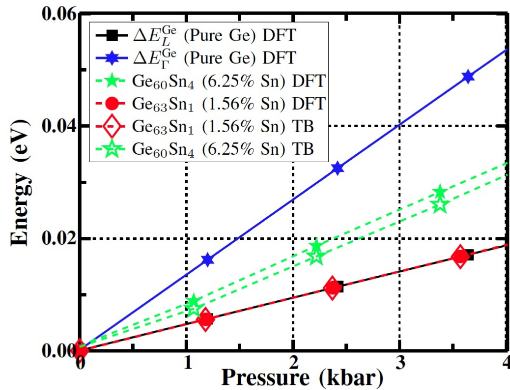

Fig. 1. Relative band gap energy shift with applied pressure. The band gap shifts for pure Ge are given by the black squares (fundamental indirect gap) and the blue hexagons (direct gap at Γ). The results for the 64 atom GeSn SC with 1 Sn atom (1.56% Sn) are given by the red symbols (diamonds,circles). The results from the cell with 4 Sn atoms (6.25% Sn) are denoted by the green symbols (stars). Open symbols: DFT data; filled symbols: TB data.

Results from sp^3s^* TB calculations are given by the open symbols and will be discussed below. The reference point for all calculations are the band gaps of the respective equilibrium structures. In addition to the results from the different GeSn SC calculations we have also performed DFT calculations for pure Ge under pressure. The extracted pressure coefficient of the fundamental Ge indirect band gap (black squares) is 4.66 meV/kbar, which is in excellent agreement with experiment (4.34 meV/kbar) [6]. For the pure Ge gap at Γ (blue hexagons) we find a pressure coefficient of 13.3 meV/kbar again in very good agreement with experiment (12.9 meV/kbar) [6]. When looking at the results from the GeSn SCs, the fundamental SC band gap (red circles) for the low Sn content (1.56% Sn), exhibits a pressure dependence very close to the coefficient of the fundamental Ge gap (CB L-states related). Thus, the $Ge_{63}Sn_1$ system (1.56% Sn) can be classified as being an indirect gap material. The situation is completely different for the $Ge_{60}Sn_4$ system with 6.25% Sn (filled green stars). Here, the pressure dependence of the GeSn band gap is neither that of the pure Ge band gap at Γ (blue hexagon) nor that of the pure Ge fundamental gap (black squares). The DFT data predicts here a pressure coefficient of 8.2 meV/kbar. Thus, our calculations reveal that band mixing effects play a central role when describing the electronic structure and especially the nature of the band gap of GeSn alloys. This conclusion is further supported when looking at the pressure dependence of the different calculated CB states with varying Sn contents (not shown here) [7]. Our results also indicate that the alloy microstructure plays an important role when looking at band mixing effects in GeSn alloys (not shown) [7]. Overall, this radically new interpretation of the evolution of the nature of the band gap in GeSn alloys is in good agreement with recent pressure dependent band gap measurements on these systems [6]. Thus, our theoretical results are in stark contrast to the perception of a sharp indirect-to-direct band gap transition as assumed in the literature.

While our HSE-DFT calculations give insight into the fundamental properties of GeSn alloys, only relatively small SCs can be targeted, due to the high computational cost. To treat GeSn alloys up to for instance 12%, large SCs are required to reduce the impact of finite size effects on the results. Also, to study the impact of the alloy microstructure on the results in all detail, the calculations have to be repeated several times on large SCs. Thus, we have established a semi-empirical sp^3s^* TB model, which is, compared to DFT, computationally less demanding. We use the results from our HSE-DFT calculations to parameterize and benchmark the TB model. Figure 1 depicts results from our TB model (open symbols), performed on the DFT-relaxed SCs. As one can see, the TB data are in very good agreement with the HSE-DFT results. This shows already that our semi-empirical model is an ideal candidate for future studies of the electronic and optical properties of GeSn alloys.

IV. Conclusion

In summary we have shown, using HSE-DFT, that the nature of the band gap in GeSn alloys is significantly affected by CB mixing effects. Our calculations indicate a continuous evolution of the band gap character, which is in stark contrast to the widely made assumption of a sharp indirect-to-direct gap transition in these alloys. Also, we discussed and presented that the obtained DFT-based understanding forms the starting point for semi-empirical atomistic studies. These models will allow to investigate larger SCs and thus to cover the impact of the alloy microstructure on the electronic and optical properties of GeSn alloys in further detail.

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