

# Comparative analysis of electronic structure evolution in $\text{Ge}_{1-x}\text{Sn}_x$ and $\text{Ge}_{1-x}\text{Pb}_x$ alloys

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**Abstract**—We present a comparative analysis of electronic structure evolution and the indirect- to direct-gap transition in  $\text{Ge}_{1-x}(\text{Sn,Pb})_x$  group-IV semiconductor alloys. We present first principles disordered alloy electronic structure calculations for  $\text{Ge}_{1-x}(\text{Sn,Pb})_x$  special quasi-random structures, and find a significantly larger band gap reduction in  $\text{Ge}_{1-x}\text{Pb}_x$  than in  $\text{Ge}_{1-x}\text{Sn}_x$  at fixed  $x$ . We calculate that  $\text{Ge}_{1-x}\text{Pb}_x$  becomes a direct gap semiconductor close to the composition ( $x \approx 7\%$ ) at which it also becomes a zero-gap semiconductor. The indirect- to direct-gap transition in  $\text{Ge}_{1-x}\text{Sn}_x$  occurs over an extended composition range, also centered around 7%, and is driven by Sn-induced mixing of Ge  $\Gamma$  and L conduction states. The pronounced band mixing effects present in  $\text{Ge}_{1-x}\text{Sn}_x$  alloys will have significant implications for optical and transport properties.

## I. INTRODUCTION

The group-IV semiconductors Si and Ge possess indirect fundamental band gaps, limiting their application in active photonic devices. Motivated by the potential to develop devices offering enhanced performance and new capabilities while remaining compatible with complementary metal-oxide semiconductor (CMOS) fabrication infrastructure, there has been a strong growth of interest in engineering the band structure of group-IV materials to achieve a direct fundamental band gap. One prominent approach is incorporation of Sn in Ge to form the  $\text{Ge}_{1-x}\text{Sn}_x$  alloy. Progress in the development of  $\text{Ge}_{1-x}\text{Sn}_x$  alloys has gathered significant pace, leading recently to demonstrations of optically and electrically pumped lasing [1], [2].  $\text{Ge}_{1-x}\text{Pb}_x$  is also attracting interest, given the recent prediction that it should become a direct gap semiconductor at low Pb compositions  $x \approx 3\%$  [3].

Theoretical calculations have revealed the hybridised nature of the alloy conduction band (CB) edge [4] in  $\text{Ge}_{1-x}\text{Sn}_x$ , and highlighted the importance of band mixing of Ge host matrix states in determining the character and evolution of the alloy band gap [5]. There have as yet been no detailed studies of  $\text{Ge}_{1-x}\text{Pb}_x$  alloys, despite that these also offer the possibility to achieve a CMOS-compatible direct-gap group-IV material. The character of CB edge states in  $\text{Ge}_{1-x}(\text{Sn,Pb})_x$  alloys has significant implications for optical and transport properties, with quantitative analysis requiring detailed understanding of the electronic structure. To develop this understanding, we present a comparative theoretical analysis of the electronic structure evolution in  $\text{Ge}_{1-x}\text{Sn}_x$  and  $\text{Ge}_{1-x}\text{Pb}_x$  alloys. We demonstrate that Sn or Pb incorporation in Ge strongly modifies the CB structure. The indirect- to direct-gap transition is driven by band mixing in  $\text{Ge}_{1-x}\text{Sn}_x$  and occurs over a range of Sn composition, but shows a more conventional evolution in  $\text{Ge}_{1-x}\text{Pb}_x$ . We calculate that  $\text{Ge}_{1-x}\text{Pb}_x$  becomes a direct gap semiconductor close to the composition ( $x \sim 7\%$ ) where

it also becomes a zero-gap semiconductor. Overall, the two alloys evolve to direct-gap semiconductors at similar Sn and Pb composition, but with the transition occurring in a more technologically relevant energy gap range for  $\text{Ge}_{1-x}\text{Sn}_x$ .

## II. THEORETICAL MODEL

Electronic structure calculations for substitutional  $\text{Ge}_{1-x}(\text{Sn,Pb})_x$  alloy supercells are carried out using density functional theory (DFT). Structural relaxation proceeds via minimisation of the lattice free energy in the local density approximation (LDA). Due to the tendency of the LDA to underestimate band gaps, electronic structure calculations for LDA-relaxed supercells are performed using the modified Becke-Johnson (mBJ) exchange-correlation functional. The semi-core  $d$  orbitals of Ge, Sn and Pb are treated as core electron states, and spin-orbit coupling is explicitly included in all calculations. All calculations are performed using the projector augmented-wave method, as implemented in the Vienna Ab-initio Simulation Package (VASP) [6]. Our combined LDA + mBJ calculations have been benchmarked against, and found to be in excellent quantitative agreement with, hybrid functional DFT calculations. Full details of this benchmarking, as well as the implementation of our DFT calculations, can be found in Ref. [5].

## III. RESULTS

Figure 1(a) shows the calculated CB structure of an ordered, 64-atom  $\text{Ge}_{63}\text{Sn}_1$  ( $x = 1.56\%$ ) supercell. Firstly, we calculate that Sn incorporation causes a reduction in the fundamental supercell band gap  $E_g$ , from 0.724 eV in  $\text{Ge}_{64}$  – the Ge fundamental (indirect) band gap in our model – to 0.660 eV in  $\text{Ge}_{63}\text{Sn}_1$ . Secondly, we find that the  $\text{Ge}_{63}\text{Sn}_1$  CB edge states, which are primarily derived from the Ge  $L_{6c}$  CB edge states, are split in energy. Of these two sets of alloy CB edge states we find that (i) the lower energy set is sixfold (threefold plus spin) degenerate and possess purely  $p$ -like orbital character at the Sn lattice site, while (ii) the higher energy set is twofold (spin) degenerate and possesses purely  $s$ -like orbital character at the Sn lattice site. The lower energy set of states retain purely Ge  $L_{6c}$  character, while the higher energy set of states are found to consist primarily of an admixture of the Ge  $L_{6c}$  and  $\Gamma_{7c}$  CB edge states. This confirms the emergence of hybridised alloy CB edge states, formed by Sn-induced mixing of the Ge  $L_{6c}$  and  $\Gamma_{7c}$  states [5]. Similar band mixing is found in an equivalent  $\text{Ge}_{63}\text{Pb}_1$  supercell – the calculated CB structure of which is shown in Fig. 1(b) – but the ordering of the states having  $s$ - and  $p$ -like orbital character at the Pb lattice site is reversed, so that the lowest energy CB

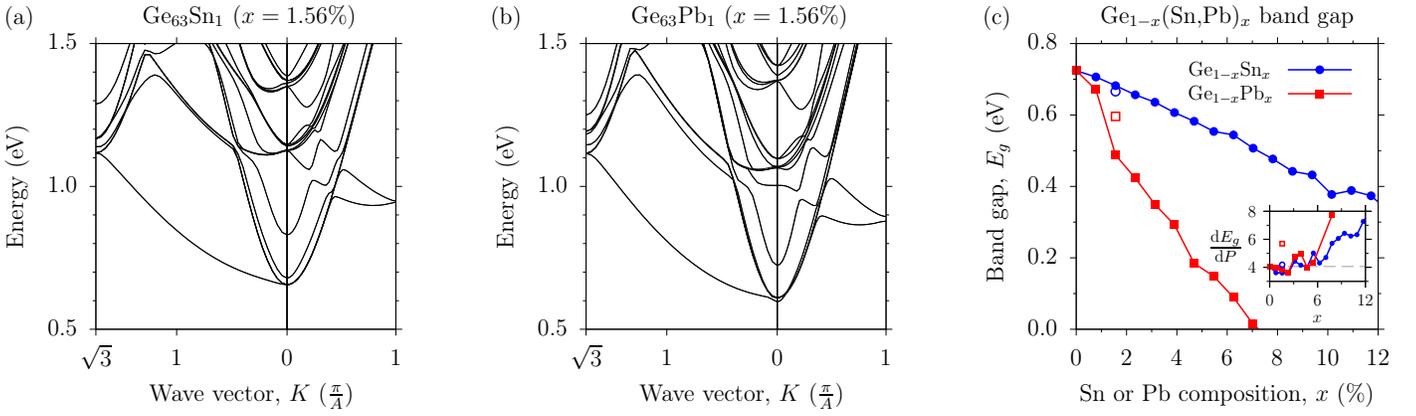


Fig. 1. CB structure of ordered, 64-atom (a)  $\text{Ge}_{63}\text{Sn}_1$ , and (b)  $\text{Ge}_{63}\text{Pb}_1$  alloy supercells. Left- and right-hand panels show the band dispersion along the (111) and (001) directions in the supercell Brillouin zone. The zero of energy in each case is set at the supercell valence band edge. (c)  $E_g$  vs.  $x$  for 128-atom  $\text{Ge}_{1-x}\text{Sn}_x$  (closed blue circles) and  $\text{Ge}_{1-x}\text{Pb}_x$  (closed red squares) SQSs. The inset to (c) shows the corresponding pressure coefficients  $\frac{dE_g}{dP}$ , in units of meV  $\text{kbar}^{-1}$ .  $E_g$  and  $\frac{dE_g}{dP}$  calculated for the ordered  $\text{Ge}_{63}\text{Sn}_1$  and  $\text{Ge}_{63}\text{Pb}_1$  supercells of (a) and (b) are shown using open blue circles and red squares, respectively.

states possess partial Ge  $\Gamma_{7c}$  character. The calculated band gap  $E_g = 0.596$  eV in  $\text{Ge}_{63}\text{Pb}_1$  is 128 (64) meV lower than that in  $\text{Ge}_{64}$  ( $\text{Ge}_{63}\text{Sn}_1$ ), demonstrating that Pb incorporation results in significantly larger band gap reduction at a given composition  $x$  than that associated with Sn incorporation.

To investigate the evolution of the band gap with  $x$  for the two alloys, we have calculated the electronic structure of a series of disordered, 128-atom special quasi-random structures (SQSs). The results of these calculations are summarised in Fig. 1(c), which shows the calculated variation of  $E_g$  with  $x$  for  $\text{Ge}_{1-x}\text{Sn}_x$  (closed blue circles) and  $\text{Ge}_{1-x}\text{Pb}_x$  (closed red squares). For  $\text{Ge}_{1-x}\text{Sn}_x$  ( $\text{Ge}_{1-x}\text{Pb}_x$ ) we calculate that  $E_g$  reduces by  $\approx 34$  meV ( $\approx 101$  meV) per % Sn (Pb) for  $x \lesssim 12\%$ . We note that incorporation of  $\approx 7\%$  Pb is sufficient to close the band gap in  $\text{Ge}_{1-x}\text{Pb}_x$ , beyond which composition the alloy becomes semimetallic. To analyse the nature of the  $\text{Ge}_{1-x}(\text{Sn,Pb})_x$  band gap we calculate the band gap pressure coefficient  $\frac{dE_g}{dP}$ . The calculated pressure coefficients of the fundamental indirect and direct band gaps of Ge are 4.1 and 13.3 meV  $\text{kbar}^{-1}$  respectively, with similar respective values to be expected for an indirect- or direct-gap alloy. For  $x \lesssim 6\%$   $\frac{dE_g}{dP}$  remains close to the Ge indirect gap value (dashed grey line in the inset to Fig. 1(c)) in both  $\text{Ge}_{1-x}\text{Sn}_x$  and  $\text{Ge}_{1-x}\text{Pb}_x$ .  $\frac{dE_g}{dP}$  then increases gradually with further increasing  $x$  in  $\text{Ge}_{1-x}\text{Sn}_x$ , reflecting a continuous transition to a direct band gap via the transfer of Ge  $\Gamma_{7c}$  character to the alloy CB edge. A much sharper increase in  $\frac{dE_g}{dP}$  is observed in  $\text{Ge}_{1-x}\text{Pb}_x$  for  $x \gtrsim 6\%$ , which is calculated to become a direct gap alloy for  $x \approx 7\%$ . Comparing the calculated values of  $E_g$  and  $\frac{dE_g}{dP}$  for the ordered  $\text{Ge}_{63}(\text{Sn,Pb})_1$  supercells of Figs. 1(a) and 1(b) (open symbols in Fig. 1(c)) with those of the disordered SQSs highlights that the nature of the band mixing which determines the energy and Ge  $\Gamma_{7c}$  character of the  $\text{Ge}_{1-x}(\text{Sn,Pb})_x$  CB edge depends strongly on the alloy microstructure.

#### IV. CONCLUSION

We have performed a comparative analysis of the evolution of the electronic structure with composition in  $\text{Ge}_{1-x}\text{Sn}_x$  and  $\text{Ge}_{1-x}\text{Pb}_x$  alloys. Despite Sn and Pb having larger covalent radius and smaller electronegativity than Ge, incorporation

of Sn or Pb in Ge primarily impacts the CB structure. Our calculations demonstrate that the evolution of the CB structure in  $\text{Ge}_{1-x}\text{Sn}_x$  is characterised by strong band mixing: Sn incorporation results in hybridisation of the CB edge states of the Ge host matrix semiconductor, with the alloy band gap then possessing neither purely direct nor indirect character. Band mixing effects are less critical in  $\text{Ge}_{1-x}\text{Pb}_x$ , where the indirect- to direct-gap transition occurs over a smaller range of  $x$ , and close to the composition at which a vanishing band gap is calculated. The emergence of a direct band gap in  $\text{Ge}_{1-x}(\text{Sn,Pb})_x$  alloys confirms the promise of these materials for practical applications. However, the hybridised nature of the alloy CB edge states in  $\text{Ge}_{1-x}\text{Sn}_x$ , and the transition to zero gap in  $\text{Ge}_{1-x}\text{Pb}_x$ , will have significant consequences for optical and transport properties, and hence for the realisation of devices based on this emerging class of semiconductor alloys.

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#### REFERENCES

- [1] S. Wirths, R. Geiger, N. von den Driesch, G. Mussler, T. Stoica, S. Mantl, Z. Ikonik, M. Luysberg, S. Chiussi, J. M. Hartmann, H. Sigg, J. Faist, D. Buca, and D. Grützmacher, "Lasing in direct-bandgap GeSn alloy grown on Si," *Nat. Photonics*, vol. 9, p. 88, 2015.
- [2] J. Margetis, Y. Zhou, W. Dou, P. C. Grant, B. Alharthi, et al., "All group-IV SiGeSn/GeSn/SiGeSn QW laser on Si operating up to 90K," *Appl. Phys. Lett.*, vol. 113, p. 221104, 2018.
- [3] W. Huang, B. Cheng, C. Xue, and H. Yang, "The band structure and optical gain of a new IV-group alloy GePb: first principles calculation," *J. Alloy. Compd.*, vol. 701, p. 816, 2017.
- [4] C. Eckhardt, K. Hummer, and G. Kresse, "Indirect-to-direct gap transition in strained  $\text{Sn}_x\text{Ge}_{1-x}$  alloys," *Phys. Rev. B*, vol. 89, p. 65201, 2014.
- [5] E. J. O'Halloran, C. A. Broderick, D. S. P. Tanner, S. Schulz, and E. P. O'Reilly, "Comparison of first principles and semi-empirical models of the structural and electronic properties of  $\text{Ge}_{1-x}\text{Sn}_x$  alloys," *submitted*, 2019.
- [6] G. Kresse and J. Furthmüller, "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set," *Phys. Rev. B*, vol. 54, p. 11169, 1996.