Short-range order in SiSn alloy enriched by second-nearest-neighbor repulsion

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Although often conceived as random solid solutions, alloys may exhibit a local short-range order (SRO) where the distribution of atoms deviates from a perfect randomness, owing to complex interactions among alloying elements. SRO can affect various properties of alloys, but understanding their exact forms, roles, and origins remains challenging from experiment alone. Here we show, through combining statistical sampling and *ab initio* calculations, that a strong and special SRO dominates the structure of SiSn alloy, which is a key subset of group IV alloys for mid-infrared technology. Remarkably, the SRO in SiSn is found to be reflected primarily by a strong depletion in the second Sn-Sn coordination shell. This is distinguished from the main character of the SRO in the closely related GeSn alloy, which is reflected by the depletion within the first Sn-Sn coordination shell. The unique nature of SRO in SiSn alloy is further attributed to the competition between the two unfavorable local configurations in SiSn: A Sn-Sn first-nearest neighbor through a direct bond and a Sn-Sn second-nearest neighbor through a Sn-Si-Sn motif. The large energy penalty induced by Sn-Si-Sn local structural motif is found to be responsible for the difference between SiSn and GeSn in their forms of SRO. The SRO in SiSn alloy is further demonstrated to substantially raise the direct band gap. Our finding thus constitutes a new knowledge of the origin and form of SRO and lays the foundation for understanding the complex structure of SiGeSn ternary alloy.

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I. INTRODUCTION

The III-V direct band-gap semiconductors have been widely used for optoelectronics, but their high cost, toxicity, and incompatibility with Si techology call for a search of alternative materials, particularly for mid-infrared applications. Group IV alloys based on Si, Ge, and Sn thus have attracted a substantial interest as a potential candidate, owing to their tunable band gaps through band-gap engineering. One promising approach to achieve direct band-gap group IV semiconducting material is through the introduction of a sufficient amount of Sn into Ge lattice [1-3]. Indeed, experimental studies have demonstrated that an indirect-to-direct transition occurs in Ge when alloyed with about 8% Sn [4-10]. Another interesting alternative is SiSn alloy [11,12], which also offers a natural compatibility with silicon technology. More importantly, mixing Si, Ge, and Sn altogether to form a ternary alloy enables a wide range of tunability of properties that can be tailored to meet the need for designing novel optoelectronic devices.

A commonly employed assumption conceives group IV alloys as random solid solutions where atoms randomly occupy diamond cubic (DC) lattice sites, with probabilities solely determined by alloy's compositions. This assumption underlies the interpretation of experimental data [13–18] and forms the basis for many theoretical predictions [12,19–32]. An issue with the random solution picture is that the possible correlations among alloying elements, which is often reflected through a short-range chemical order (SRO), is neglected.

Indeed, SRO has been recently identified in metallic [33,34], semiconducting [35,36], and oxide alloys [37], which was found to play a decisive role controlling mechanical, thermoelectric, and ion transport properties of materials. In group IV alloy systems, characterization studies also showed the local atomic configurations in GeSn [38,39], and SiGeSn [40,41] alloys display a deviation from a truly random distribution, thus prompting the question as to how random these alloys truly are. In our recent theoretical study [42], we have thoroughly examined this question in both SiGe and GeSn alloy by employing Monte Carlo sampling combined with density functional theory (DFT) calculations. The study [42] indeed showed that while SiGe is nearly a random solid solution, GeSn alloy exhibits a clear SRO, mainly reflected by a substantially lower Sn-Sn 1st coordination number (1CN) than that of a truly random alloy. The SRO was further found to significantly impact electronic properties of GeSn alloys, enabling an improved prediction of electronic band gaps.

The study naturally prompts a similar question in SiSn alloy, which is one of the three pillar binary alloys constituting the Si-Ge-Sn ternary system. The electronic properties of SiSn alloy can be tuned by varying the composition of Sn in a way similar to GeSn alloy, albeit that the required Sn composition to achieve an indirect-to-direct transition may be substantially higher [22], owing to the greater direct band gap of the hosting DC Si. Despite this potential, SiSn has not been investigated as extensively as the other two alloys, i.e., SiGe and GeSn, mainly because of the challenges in synthesis due to the low solubility of Sn in Si [43]. However, recent experimental studies have demonstrated the possibility of achieving a high-Sn content of $20 \sim 25\%$ in SiSn alloy [11,12]. More

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importantly, as a key suballoy system for the more-interested Si-Ge-Sn alloy, gaining a fundamental insight into both the structure and the property of SiSn alloy is required for understanding and designing the SiGeSn ternary alloys. In particular, it is critical to understand whether SRO also exists in SiSn and if it does, how much it affects the properties of SiSn and potentially interacts with the SRO within GeSn when SiGeSn alloy is formed.

To address these questions, we investigate the structure and electronic properties of SiSn alloys by conducing statistical sampling at the DFT level. Our study indeed shows that a strong SRO exists in SiSn alloy, as in fact expected from our previous understanding of the SRO in GeSn alloy. Intriguingly, the SRO in SiSn is found to exhibit a very different nature from that in GeSn, in that Sn atoms tend to avoid each other in both their first and their second coordination shells, particularly in the second. This is in contrast to the behavior of GeSn where Sn atoms tend to repel each other only in their first coordination shell. The competition between the two repulsive interactions through Sn-Sn first-nearest neighbor (1NN) and Sn-Sn second-nearest neighbor (2NN) yields a more complex structure in SiSn, which is further found to significantly affect the alloy's electronic properties.

II. METHODS

A. DFT-based Monte Carlo sampling

To obtain the ensemble average of the properties, e.g., CN, calculated based on different atomic configurations through a canonical sampling, we adopt the Metropolis Monte Carlo method [44] where the acceptance probability for a new configuration *j* generated from a trial move from a configuration *i* equals to min $\{1, \exp(-(E_j - E_i)/k_BT)\}$, where E_i and E_j are the total energies of configuration *i* and *j*, respectively, k_B is the Bolzmann constant, and *T* is temperature (set to be 300 K). For each trial move, a pair of solute and solvent atoms are randomly selected and swapped to create a new configuration *j*, which then undergoes a full relaxation to obtain its energy E_j . About 3000 to 8000 MC moves are used to sample each alloy composition to ensure the convergence in the calculated CNs [42].

The total energy E is calculated based on DFT, implemented in the Vienna ab initio simulation package (VASP) [45] based on the projector augmented wave method [46-48]. Local density approximation (LDA) [49] is employed for the exchange-correlation functional, as previous studies [28,30,50,51] showed LDA yields the best agreement with experiment on Sn for geometric optimization. A simulation cell containing 64 atoms is generated by replicating a conventional 8-atom DC cell twice along each dimension. An energy cutoff of 300 eV and a $2 \times 2 \times 2$ Monkhorst-Pack k-points grid [52] are chosen for structural relaxation, combined with the convergence criteria of 10^{-4} and 10^{-3} eV for electronic and ionic relaxations, respectively. The choice of these parameters is carefully tested to ensure the total energy difference $\Delta E = E_i - E_i$ between two configurations *i* and *j*, which is of central importance for MC sampling, is well converged; see Supplemental Fig. S1 [53] for details of the convergence test. To cross-validate the results against size and shape effects, a supercell containing 128 atoms, which is generated by replicating the primitive cell of DC four times along each dimension, is also used for MC sampling. To achieve higher computational efficiency of sampling based on a 128-atom cell, only gamma point is used to sample the Brillouin zone. The test on the calculated Sn-Sn 1CN (see Supplemental Fig. S2 [53]) shows that our results are robust against the change of simulation shape and size. Except for band-structure calculations (see below), all of our results are reported based on a 64-atom cell.

B. Radial distribution function

Sn-Sn radial distribution function (RDF) for SRO-SiSn alloy is obtained by first randomly choosing 600 snapshots from the obtained MC trajectory based on a 64-atom cell (excluding the first 500 configurations due to equilibration), followed by conducting *ab initio* molecular dynamics (AIMD) at 300 K for 1 ps on each configuration to account for thermal motion of atoms, then calculating Sn-Sn RDF based on the AIMD trajectory with a total length of 600 ps. AIMD is carried out using Gamma point sampling. The RDF of a random SiSn alloy is obtained in a similar fashion, but based on 600 randomly generated configurations which are first fully relaxed, then followed by AIMD. Sn-Sn 1CN and 2CN are calculated through integrating the calculated Sn-Sn RDF from 0 to the first local minimum and from the first to the second local minima, respectively.

C. CN-energy correlation map

To explore the correlation between Sn-Sn CN and total energy, we employ the SciPy package [54] through the module scipy.stats.binned_statistics. The entire energy range is evenly divided into 100 bins and the averaged Sn-Sn CN for each bin is calculated based on all the configurations collected in MC or random sampling with their energies falling within the range of the bin.

D. Band-structure calculations

To overcome the well-known band-gap problem of LDA, modified Becke-Johnson (mBJ) exchange potential [51] is employed for band-structure calculations. Previous studies [28,30] have shown that a *c*-mBJ parameter of 1.2 reproduces the correct band gaps for α -Sn and Ge. Our test also shows this c-mBJ parameter predicts the direct band gap of pure Si to be 3.34 eV, in good agreement with the experimental value \sim 3.45 eV [55]. To obtain a meaningful band structure of alloy based on supercell, we apply the spectral weight approach [56,57] to recover the Bloch character of electronic eigenstates perturbed by disorder by unfolding the band structures of a primitive-based 128-atom cell back into the first primitive Brillouin zone of a DC lattice. The band unfolding is carried out by employing the code *fold2bloch* [57]. Spin-orbit coupling (SOC) is included in the band-structure calculation, as SOC was demonstrated to be crucial for reproducing the band structure of α -Sn [28,30], which is also expected to strongly affect the electronic structure of Sn-based alloy.



FIG. 1. Calculated ensemble average of (a) Sn-Sn 1CN and (b) Sn-Sn 2CN as a function of Sn concentration in GeSn and SiSn alloy at 300 K. The data for Sn-Sn 1CN in GeSn are obtained from Ref. [42].

III. RESULTS

A. Structural signature of SiSn alloy

The substantially lower-than-ideal Sn-Sn 1CN in GeSn was partially attributed to the large size difference (14%) between Ge and Sn atoms, because the size mismatch makes it energetically less favorable to have Sn-Sn nearest neighbors within the DC lattice of Ge [42]. Given this understanding, and considering the even greater size difference (19%) between Si and Sn atoms, SiSn alloy is expected to exhibit a strong SRO, potentially through an even lower Sn-Sn 1CN. To test this hypothesis, we carried out a DFT-based MC sampling of SiSn alloy. As shown in Fig. 1(a), the calculated Sn-Sn 1CN is indeed found to be lower than that of a random solution, but in contrast to the expectation, higher than that in GeSn alloy. In fact, except for a low Sn composition (<20%), the calculated Sn-Sn 1CN is found to be quite close to that of a truly random alloy, particularly for a Sn composition beyond 40%.

To examine whether this behavior implies SiSn alloy is best represented by a random solid solution model, we then carry out a random sampling study where more than 3000 configurations are randomly generated for each composition to compute a simple arithmetic average of the total energy $E_{\rm ran}$. If an alloy were a random solid solution, then $E_{\rm ran}$ would be identical to the canonical ensemble average of total energy $\langle E_{\rm can} \rangle$ obtained through MC sampling. Indeed, this is found to be the case for SiGe alloy over the entire composition range (see Supplemental Fig. S3 [53]), confirming the applicability of a random solution model in describing the structure of SiGe alloy. GeSn alloy, on the other hand, has a $\overline{E_{ran}}$ significantly greater than $\langle E_{can} \rangle$, indicating that a random configuration of GeSn is energetically less favorable, which is a signature of SRO. Importantly, such an energy difference $(\overline{E_{ran}} - \langle E_{can} \rangle)$ for SiSn alloy is further found to be nearly twice as that in GeSn. The strong energy decrease identified in canonical samplingand thus clearly suggests SiSn is not a random solid solution.

The large energy difference $\overline{E_{\text{ran}}} - \langle E_{\text{can}} \rangle$, along with the close-to-ideal Sn-Sn 1CN, indicates the SRO of SiSn alloy bears a different character from that of GeSn. To understand the structural signature of SRO in SiSn alloy, we investigated the solute-solute distribution beyond the first coordination

shell. As shown in Fig. 1(b), SiSn alloy indeed exhibits a significant reduction in the calculated Sn-Sn 2CN with respect to the corresponding value of a random alloy. The contrasting behaviors of Sn-Sn 1CN and 2CN can be further illustrated by the calculated Sn-Sn RDF. As shown in Fig. 2, in a low Sn-content SiSn alloy, e.g., 12.5% Sn, both the first and the second Sn-Sn peaks are significantly suppressed with respect to a random distribution, leading to a depletion of Sn atoms in both the first and second coordination shells. Such depletion is largely compensated by the enhancement of the third Sn-Sn peak. As Sn composition increases, e.g., 37.5%, the difference between the SRO and the random alloy in the first Sn-Sn peak diminishes, leaving only the second Sn-Sn peak significantly reduced. In comparison, the Sn-Sn 2CN in GeSn alloy only displays a very small deviation from a random distribution [42]. Therefore, the analysis shows the SRO in SiSn is reflected by the depletion of solute-solute CN in both *first* and second coordination shells at a low Sn composition and only the *second* coordination shell at a high Sn composition. This behavior is fundamentally distinct from the nature of SRO in GeSn alloy.

B. Origin of SRO in SiSn

The result leads to the question of how the solute-solute 1CN and 2CN are related to the energetics of SiSn alloy. To this end, we analyze the correlation between the number of solute-solute nearest neighbors and the calculated total energy obtained in MC sampling. Figure 3 (lower panel) shows there indeed exists a general, positive correlation between solutesolute 2CN and energy at different Sn compositions. We note that the main carrier of solute-solute 2CN in a DC lattice is a local solute-solvent-solute motif, e.g., Sn-Si-Sn. Such correlation thus suggests the local solute-solvent-solute configuration is energetically unfavorable in SiSn alloy. In contrast, the positive correlation between 1CN and energy is only found in SiSn alloy with a Sn composition below 25%, beyond which such correlation disappears, as shown in Fig. 3 (upper panel, solid circles). The lack of correlation between solute-solute 1CN and energy suggests that, in the low-energy range, the further decrease in the energy of SiSn alloy in MC sampling is no longer due to a further reduction of Sn-Sn 1CN when a Sn



FIG. 2. Calculated Sn-Sn RDF of SiSn alloy with SRO (red) and random solid solution (black) for different Sn compositions.

composition is beyond 25%. This analysis is thus consistent with the nearly random distribution of Sn-Sn 1NN for this composition range identified in Fig. 1(a). However, it should be noted that the lack of correlation between Sn-Sn 1CN and energy in SiSn should be interpreted only within the context of MC sampling, where the distribution of atoms is found to be not random. For a truly random distribution, as we further examine through a random sampling, such positive correlation indeed recovers, as shown by the open circles in Fig. 3. Since MC sampling only visits the most probable structures of SiSn alloy, the energy range it visits is typically concentrated in the lower energy domain. In contrast, a random sampling is more likely to create energetically very unfavorable structures, for example, a larger Sn cluster, thus leading to an energy range spanning the high-value domain. The recovery of the positive correlation between 1CN and energy in random sampling indicates that a Sn-Sn 1NN is indeed energetically unfavorable, similar to Sn-Sn 2NN. The analysis shows that the role of Sn-Sn 1CN, however, becomes less important when Sn composition is high enough for SiSn alloy with SRO. In contrast, GeSn alloy is found to exhibit a clear, positive correlation between Sn-Sn 1CN and energy (see Supplemental Fig. S4 [53]) throughout the wide composition range, highlighting the generic role of Sn-Sn 1NN in determining the energy of GeSn alloy regardless of composition.

Motivated by this analysis, we further calculate the energy increase dE due to the formation of a Sn-Sn neighbor by bringing together two Sn atoms that were further apart [corresponding to the sixth-nearest neighbor (6NN)] within the host lattice, as shown in Fig. 4. For GeSn, our calculation shows the energy difference of a Sn-Sn 1NN with respect to a 6NN ~0.108 eV, which is significantly higher

than that of a Sn-Sn 2NN (~ 0.031 eV). The high-energy cost of creating a Sn-Sn 1NN thus makes it energetically unfavorable in GeSn alloy, which is consistent with our previous finding that SRO in GeSn is mainly reflected through a depletion of Sn-Sn 1CN. In contrast, the *dE* for Sn-Sn 1NN (~ 0.101 eV) and 2NN (~ 0.079 eV) in SiSn are found to be both large and comparable. In particular, the virtual degeneracy in their energy costs indicates both Sn-Sn 1NN and 2NN are energetically unfavorable in SiSn alloy.

We note that in a DC lattice, each atom has four 1NN and 12 2NN. If Sn atoms randomly replace Si atoms in the lattice, then the possibility of forming a Sn-Sn 2NN configuration is naturally higher than that of forming a Sn-Sn 1NN. Assuming the formation energies of Sn-Sn 1NN and 2NN are identical, and the total energy is a superposition of energies from various local configurations, i.e., neglecting coupling effect, one can conceive that a SiSn alloy may lower its energy through minimizing both solute-solute 1CN and 2CN simultaneously. Such minimization can be at work at a low solute composition, where there are a smaller number of solute atoms in the lattice so that the two minimization processes could proceed independently and simultaneously, i.e., eliminating a local configuration of one type, e.g., a Sn-Sn 1NN, without necessarily creating configurations of another type, e.g., a Sn-Sn 2NN. Indeed, we observe that the Sn-Sn 1CN and 2CN in SRO SiSn alloy are both significantly lower than the corresponding ideal values for a random alloy when Sn composition is below 25%, as shown in Fig. 1. However, when Sn composition increases, the two minimization processes become mutually exclusive: Reducing the number of one type of Sn-Sn NN can well be at the expense of increasing



FIG. 3. Correlation map for Sn-Sn 1CN and energy (upper panel) and Sn-Sn 2CN and energy (lower panel), in SiSn alloys for different Sn compositions. Correlation map is obtained based on both MC sampling (solid circle) and random sampling (open circle), by grouping energy data collected from sampling trajectory into a total of 100 bins (see Methods for details).



FIG. 4. Change of energy dE due to the formation of a Sn-Sn 1NN (circled red) and Sn-Sn 2NN (circled blue) in the matrix of (a) Si and (b) Ge. Formation of Sn-Sn 1NN is nearly equally unfavorable in both Si (dE = 0.101 eV) and Ge (dE = 0.108 eV) lattices, whereas the formation of a Sn-Sn 2NN in Si lattice (dE = 0.079 eV) is energetically much more unfavorable than in Ge lattice (dE = 0.031 eV).

the other type of Sn-Sn NN, because the number of sites available to simultaneously avoid both types of Sn-Sn NNs becomes scarce when a substantial number of lattice sites are already occupied by Sn atoms. In particular, eliminating one Sn-Sn 1NN by placing two Sn atoms further apart in a DC lattice will be likely to yield more than one Sn-Sn 2NN, because of the higher probability of forming a Sn-Sn 2NN. Similarly, reducing Sn-Sn 2CN can be more effective in decreasing the total energy in such case. Indeed, the SRO SiSn alloy with a Sn composition greater than 25% is found to be reflected by a substantially lowered Sn-Sn 2CN, which is further found nearly equal to that of Sn-Sn 1CN (see Supplemental Fig. S5 [53]).

Clearly, a fundamental difference that distinguishes GeSn and SiSn in their corresponding characters of SRO is that a Sn-Sn 2NN is energetically much more unfavorable within the lattice of Si than in Ge. A plausible explanation for this difference can be related to the energy cost of a local distortion induced by alloying atoms. We note that the lattice mismatch between Si and α – Sn (19%) is already greater than that between Ge and $\alpha - \text{Sn}$ (14%). Therefore, a larger local distortion can be expected when Sn atoms substitute Si atoms by forming a local Sn-Si-Sn configuration. The greater local distortion not only is reflected by the larger magnitude of the induced bond-length change (-2.49%) for Si-Sn bond, compared to -2.06% for Ge-Sn bond) but also includes a greater deviation from a perfect tetrahedral arrangement around the center Si atoms. The local tetrahedral order can be quantified by the local bond order parameter q_3 [58–60], which varies between -1 and 1, with -1 corresponding to the perfect tetrahedral order. Indeed, a local Sn-Si-Sn configuration is found to lead to a greater deviation of tetrahedral order $(\Delta q_3 = 0.00317)$ than that from Sn-Ge-Sn ($\Delta q_3 = 0.00154$). To this end, we note that although Ge and Si both form tetrahedral crystals through covalent bonding, there is an important difference in the tetrahedral strength, often termed as tetrahedrality, which measures the energy penalty for a deviation from perfect local tetrahedral configuration [61]. The higher tetrahedrality of Si, combined with the higher degree of local distortion, thus makes a local Sn-Si-Sn configuration more unfavorable than Sn-Ge-Sn.

C. Effects of SRO on direct band gaps of SiSn alloys

A critical property of interest for SiSn alloy is its electronic band gaps, which are the crucially needed parameters for device design. For GeSn alloy, it has been shown the proper inclusion of SRO in structural models leads to a significantly improved prediction on alloy's band gap, enabling an agreement with experiments [42]. To understand whether SRO also affects SiSn alloy's electronic properties, we investigate the direct band gap of SiSn alloys E_g^{Γ} . The canonical average of direct band-gap $\langle E_g^{\Gamma} \rangle$ is calculated by averaging 50 configurations randomly selected from the obtained MC trajectory. Since such an average properly accounts for the statistical weight of each configuration, $\langle E_g^{\Gamma} \rangle$ reflects the direct band gap of SiSn alloy with a SRO. In comparison, the direct band gap of a truly random SiSn alloy, $\overline{E_g^{\Gamma}}$, is obtained through averaging E_g^{Γ} of 50 randomly generated configurations.



FIG. 5. The role of SRO on the direct band gap of SiSn alloy. A canonical sampling (left column) accounting for SRO leads to an ensemble-averaged direct band-gap $\langle E_g^{\Gamma} \rangle$ significantly higher than the simply averaged band-gap $\overline{E_g^{\Gamma}}$ through random sampling (right column) for both (a) Si_{0.875}Sn_{0.125} and (b) Si_{0.75}Sn_{0.25}. The mean values are represented by the horizontal lines.

As shown in Fig. 5, the calculated direct band-gap $\langle E_g^{\Gamma} \rangle$ of a SiSn alloy with a SRO is indeed found substantially higher than $\overline{E_g^{\Gamma}}$ of a random alloy. For a Sn composition of 12.5%, the difference in the direct gap of SiSn alloy, i.e., $\langle E_g^{\Gamma} \rangle - \overline{E_g^{\Gamma}}$, is found to be 327 meV. We note that this difference is significantly greater than that (~100 meV) for the GeSn alloy of the same Sn composition [42], namely, Ge_{0.875}Sn_{0.125}, suggesting SRO in SiSn plays an even greater role in affecting alloy's electronic properties. The greater impact of SRO on the band gap is not unexpected, as SRO in SiSn modifies Sn-Sn local environment to a greater degree (i.e., both 1NN and 2NN in SiSn, as opposed to 1NN only in GeSn), which consequently leads to a larger decrease of total energy. Indeed, as Sn composition increases, our calculation shows that the difference between $\langle E_g^{\Gamma} \rangle$ and $\overline{E_g^{\Gamma}}$ grows to 420 meV [Fig. 5(b)].

IV. DISCUSSION

Our study thus demonstrates that SiSn alloy is far from being a random solid solution by showing that a strong shortrange order of atoms is preferred in the alloy. In a certain sense, the identification of SRO in SiSn is not totally unexpected, given that SRO was also recently found in GeSn alloy, which is another closely related group IV binary alloy [42]. However the SRO in SiSn exhibits a unique nature that leads to at least three major implications. First, the competition between the 1NN repulsion and the 2NN repulsion constitutes a new origin of SRO. A main reason for SRO in alloy is that alloying elements of different types often attract or repel each other due to the difference in their chemical and physical nature. Since the interaction embodies itself the strongest often through the nearest neighbor, a SRO is usually reflected by a significant change in the first coordination shell [62]. This change correspondingly induces subsequent changes in other coordination shells, e.g., the second or third, which are considered as passive changes to conserve the total number of atoms. In contrast, the SRO in SiSn proceeds through two independent repulsive interactions (Sn-Sn 1NN and 2NN) that are both at work simultaneously in the alloy when there is sufficient room to avoid both, as in the low-Sn SiSn alloy. In this case, the changes in 1CN and 2CN are not at the expense of the other. When there are not enough sites to accommodate both types of repulsion, as Sn composition increases, the two interactions must compete, which yields a different and complex manifestation of SRO. To this end, this finding constitutes a new understanding of the origin and form of SRO in alloys. Second, the SRO in SiSn has an important implication on alloy's properties. One such property of particular interest is the critical composition for an indirect-to-direct transition. This transition was previously predicted to be within a wide range of Sn content between 25 and 55% [12,22,63]. The significant impact of SRO on the direct band gap, as shown in our study that indicates a clear structure-band gap relation, thus well suggests that a revised prediction of the critical composition is needed through explicitly accounting for SRO. Such a refined prediction will provide a more reliable guidance for material growth targeting specific electronic properties and also serves as a benchmark for identifying the underlying structures of SiSn alloy. To this end, we note that although the synthesis of high-Sn content of SiSn alloy remains challenging, promising experimental approaches, e.g., solid-phase epitaxy [64], do exist to tackle this problem. Third, since both GeSn and SiSn exhibit a SRO, albeit of different forms, it is naturally expected that the two types of SRO in GeSn and SiSn can interact with each other in a ternary Si-Ge-Sn alloy. The resulted structure may thus exhibit a profound and complex local short-range order, which is further expected to be potentially different from the SRO identified in the binary alloys because of possible coupling among them. To this end, we note that there was already experimental evidence showing a SRO in Si-Ge-Sn alloy [40,41].

Last, we also note that our study pertains to equilibrium distribution at room temperature. Since the growth of group IV alloys, which is often carried out at higher temperature and driven by kinetics, may produce a distribution either close to or far from equilibrium, the degree of SRO may be expected to vary in samples prepared through different growth methods. Nevertheless, the SRO discovered in our study represents an

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inherent structural signature of group IV binary alloy which can fundamentally affect alloy's properties. In particular, the identified significant change of band gaps with alloy structure may help rationalize the variations in the measured electronic properties for the same composition and, more importantly, may help establish a link between structure and electronic properties.

V. CONCLUSION

In summary, by combining Monte Carlo sampling with DFT calculations, we demonstrate that SiSn binary alloy exhibits a strong SRO, leading to a structure significantly distinguished from a random solid solution. Our study further shows that the identified SRO in SiSn alloy is primarily characterized by a depletion of Sn-Sn 2NN, combined with a depletion of Sn-Sn 1NN, which is prominent only in low-Sn alloy. This behavior is found to be in sharp contrast to the SRO in the closely related GeSn alloy, where SRO is only reflected by Sn-Sn 1NN depletion. The unique manifestation of SRO in SiSn alloy is further found to be attributed to the collective interaction between the two unfavorable local configurations: (1) A solute-solute nearest neighbor, e.g., Sn-Sn bond, and (2) a solute-solvent-solute motif, e.g., Sn-Si-Sn configuration. The competition between the two types of unfavorable local configurations yields a structure-composition dependence, which is found to be more complex than GeSn alloy and to yield a significant change in SiSn's electronic structures. Our findings not only feature the essential role of SRO in future predictions on SiSn but also provide new physical insights to understanding of SRO in group IV alloy, preparing for future investigations on more complex SiGeSn ternary systems.

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