Empirical tight-binding simulations for nonuniform disordered GaAsSb alloy

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***Abstract*—We theoretically study the direct gap and the band-edge wavefunctions' localization of nonuniform disordered GaAsSb alloy by using empirical tight-binding simulations. We show that the nonuniformity decreases the direct gap value of the alloy while increases its statistical scattering, leading to a larger bandgap bowing compared to the ideal random alloy case. Moreover, the localization of the band-edge hole wavefunction is also enhanced due to the nonuniformity, while the band-edge electron does not experience similar effect.**

***Index Terms*—ETB, alloy, nonuniformity, localization**

I. Introduction

The nice properties of $GaAs_{1-x}Sb_x$ and related materials [1] have paved the way for various practical applications [2], [3]. As a ternary alloy, the ratio of the binary compounds and the arrangement of As and Sb anions in the lattice will determine the electronic properties of a specific material sample. The former attribute can be characterized by the compositional fraction x of Sb which ranges from 0 (pure GaAs) to 1 (pure GaSb), while the latter can be described via the uniformity level y whose range is $0 < y \leq 1$, where $y = 1$ corresponds to a spatially uniform random distribution of As and Sb anions over the whole alloy sample (known as random alloy). $y = 0$ would correspond to a highly clustered alloy. While the alloy composition x is controllable during material growth and can therefore be used to tune device properties, the uniformity might be hard to control in practice and depends on growth technique and various parameters.

From the theoretical point of view, an ideal description of such alloys requires atomistic-scale simulations of large supercells (containing $\sim 10^4{-}10^5$ atoms) in which the ions are distributed according to some probability distribution. Therefore, for the given pair of values (x, y) many simulations over different possible configurations are needed to ensure the result is statistically reliable. Using *ab initio* methods like density functional theory (DFT) becomes extremely computational expensive, if not impossible. In such situations, the empirical tight-binding (ETB) method emerges as a good candidate for balancing numerical reliability and computational expenses. Vice versa, the complexity of the spatial strain profile and atomic arrangement in alloyed materials make these systems stringent test cases for any ETB model ever proposed.

In this work, we use a modified version of the ETB scheme in [4] to calculate the direct gap of bulk GaAsSb alloys with various composition x and uniformity level y. We are also interested in the spatial distribution of the wavefunctions of the valence band-edge (VBE) state and the conduction band-edge (CBE) state. From these analyses, we can draw some preliminary conclusions on the effect of alloy composition and alloy uniformity on electronic and optical properties.

II. Theoretical model

The original ETB scheme in [4] is a $sp3d5s^*$ first-nearest-neighbor model following the framework of [5]. In this model, the ETB parameters obtained by fitting to DFT bulk band structures are associated with each pure material. Consequently, the onsite parameters and spin-orbit coupling (SOC) parameters of the same species, e.g. Ga, are different in GaAs and GaSb. This raises a natural question in the situations of alloyed systems: Which parameter set should one use for, say, Ga cations in GaAsSb? The simplest workaround is probably to average the two sets of Ga onsite (and SOC) parameters for GaAs and GaSb (also taking the valence band offset (VBO) into account) according to the first-nearest neighbors surrounding each Ga cation, which has been used in [6], [7]. Namely, if a Ga cation has bonds with n As anions and $(4{-}n)$ Sb anions, then its onsite parameters are linearly interpolated by $E_{Ga} = [nE_{Ga,GaAs} + (4-n)E_{Ga,GaSb}]/4$.

We carried out simulations for $GaAs_{1-x}Sb_x$ supercells of size $12 \times 12 \times 12$ nm^3 with x spanning the full range of composition. For a given composition, the various levels of uniformity y from 50% to 100% are considered. To ensure

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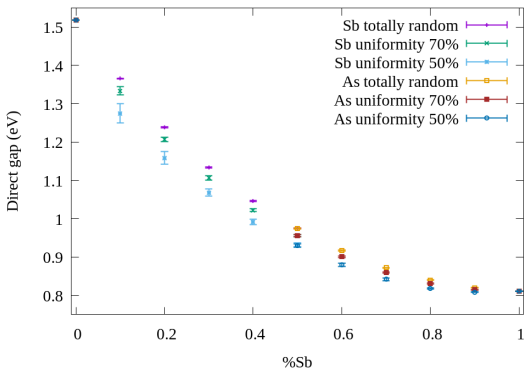

Fig. 1. The mean values (and the standard deviations) of direct gap versus Sb-composition for different levels of Sb- and As-uniformity.

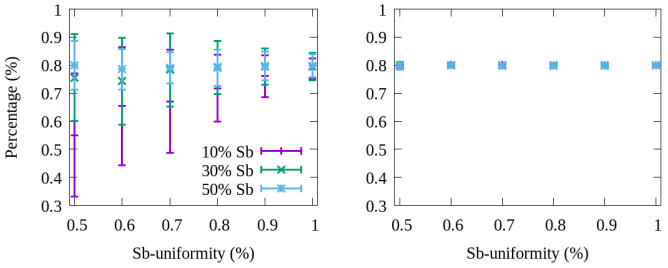

Fig. 2. The percentage of number of atoms contributing to 80% density of the VBE and CBE wavefunction versus the Sb-uniformity level for different Sb-concentration from 0.1 to 0.5.

statistical meaning, we performed the calculations on 30 different configurations for each pair of (x, y) then took the mean values and standard deviations. Regarding the construction of random nonuniform GaAsSb supercells, depending on whether the alloy is As-rich ($x \leq 0.5$) or Sb-rich ($x \geq 0.5$), we choose the anions for controlling the nonuniformity level. For example, in the case $(x = 0.1, y = 0.8)$ first 80% of Sb anions will be distributed uniformly throughout the supercell. Then, the remaining 20% of Sb anions will be placed in the anion sites with probability proportional to the number of Sb anions that are already present up to the second-nearest anion site. The other anion sites are filled up by As anions.

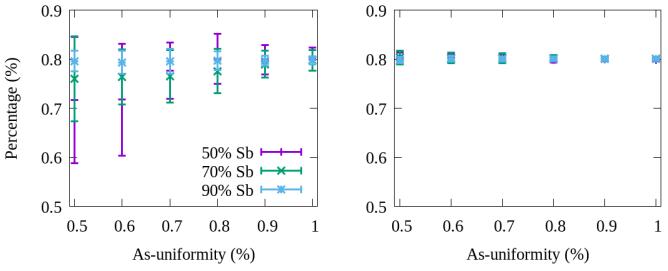

Fig. 3. Similar to Fig. 2 but versus As-uniformity for Sb-concentration from 0.5 to 0.9.

III. Simulation Results

In Fig. 1 we show the variation of the direct gap of GaAsSb with respect to Sb-composition for various uniformity levels. One can see that the uniformity level of both types of anions affects the direct gap in a way decreasing the gap values while increasing its statistical scattering. The gap bowing hence tends to increase as well. In the As-rich regime, the effect of Sb-nonuniformity is stronger than that in the medium range of x, demonstrated by both the larger difference in the mean values and the larger standard deviations. This suggests that any nonuniformity of Sb anions in the experimentally grown GaAsSb alloy could lead to a lower direct gap (hence, a higher bowing) than the value assumed for the ideal randomn case. There is no symmetry in the case of the As-nonuniformity in Sb-rich regime. The manifestation of As-nonuniformity is weaker than in the medium range of Sb-composition.

To have an idea of how the VBE and CBE wavefunctions are localized due to the nonuniformity of anions, we also calculated the partial density of state (PDOS), then obtain the percentage of atoms that are the top contributors to 80% of the density of VBE and CBE states. These percentages are shown in Fig. 2 and Fig. 3 for As-rich and Sb-rich structures, respectively. A small percentage indicates a high degree of localization of the wavefunction. One can see that both Sb- and As-nonuniformity tend to enhance the localization of the VBE wavefunction, while have almost no effect on the localization of the CBE wavefunction. This is reasonable because GaAs and GaSb have a fairly large VBO, and the hole effective mass is larger. Thus, in presence of nonuniformity, clusters of GaSb and GaAs may form and play the roles of local potential wells and barriers, acting as traps to the holes. On the other hand, since the CBEs of GaAs and GaSb are nearly aligned with each other, the local potential variation is not strong enough to localize electrons. Consequently, the impact of nonuniformity on the spatial localization of the electrons is almost negligible, manifested by the fact that approximately 80% of the atoms contribute 80% CBE density.

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