Thermal expansion of III–V materials in atomistic models using empirical Tersoff potentials

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A method to achieve realistic values for the thermal expansion coefficient in atomistic simulations of III–V materials using empirical Tersoff potentials is reported. The acceptance criterion of the Metropolis Monte Carlo algorithm that is used to relax the structures is modified to suppress exceedingly high thermal expansion, which has previously been observed for Tersoff potentials of III–V materials. Compared with earlier works, the error is reduced from more than 200% to ~3% for GaAs. Similar behaviour is found for other binary III–V compounds with errors typically around 10% with respect to the experimental data.

Introduction: Atomistic models of semiconductor materials bridge the gap between ab-initio density functional theory (DFT) methods and continuum simulations [1]. Since chemical bonds are simplified through empirical potential functions, the computational effort is dramatically reduced, while still keeping the atomic structure in contrast to continuum models such as Schrödinger-Poisson or Green’s function solvers, which rely on averaged material parameters [2, 3]. This allows us to study the effects such as local strain or interface roughness, which become significant with the downscaling of electronic devices, but which would not be accessible with DFT due to the large number of atoms required [4].

The structural properties of common elemental and III–V semiconductors, which crystallise in a diamond or zincblende lattice, can be modelled at an atomistic level using the Tersoff potential, where parameter sets are readily available [5–8]. These potentials were also proven to be reliable regarding the elastic behaviour or bond length distributions in binary compounds as well as random and spontaneously ordered ternary structures [9–12]. Such models were recently also extended to describe the behaviour of dopant atoms in III–V materials [13].

Most structural modelling works only deal with a constant temperature of either 0 or 300 K, but do not take thermal expansion and the resulting strain into account. Some works, which investigated the temperature dependence of III–V materials using Tersoff potentials, revealed a significant overestimation of the thermal expansion coefficients compared with the experimental values [8]. Yet an accurate description of thermal expansion and strain is imperative for the implementation of diffusion or epitaxial growth processes on an atomistic level. This Letter provides a modified Metropolis Monte Carlo (MMC) scheme, which is shown to be a key step towards accurate structural models at elevated temperatures.

Method: Initially, all atoms were placed in cubes of ideal zincblende lattices with an edge length of six unit cells, if not mentioned otherwise. Finite-size effects were prevented by periodic boundary conditions in three dimensions. The structures were then allowed to relax through aMMC solver, using random moves of individual atoms as well as scaling of the whole simulation box [14, 10]. A minimum of more than 50 random actions per atom was applied before evaluating data at each temperature step, although convergence was typically already achieved after 25 trials per atom.

Random actions, which lead to an increase of the bond energy, are accepted at a finite probability, according to term 1, where \( \exp \) is the difference in energy between initial and final states, and \( k_B T \) corresponds to the thermal energy. The dependence on the Boltzmann scaling factor (BSF) \( \eta \) will be discussed in the following paragraphs:

\[
P(0, 1) < \eta \exp \left( \frac{-\Delta E}{k_B T} \right) \rightarrow \text{accept} \tag{1}
\]

The averaged bond length for GaAs at different temperatures and different BSFs is plotted in Fig. 1. Data are collected from five independent simulation runs, where the slope for thermal expansion is fitted between 200 and 500 K. The case of \( \eta = 1.0 \) corresponds to the classic MMC algorithm. A significant overestimation of the thermal expansion, leading to errors of more than 200%, is inherent due to the curvature of the potential function around its minimum, which is fitted to reproduce the elastic material parameters best [6, 7]. Additionally, the potential is missing long-range attractive Coulomb forces, which may cause increased thermal expansion. While the data points for \( \eta = 0.2 \) and 0.5 show an excellent reproducibility between the different runs, a value of \( \eta = 1.0 \) leads to some spread.

The relation between the thermal expansion coefficient and the BSF appears to be non-trivial. We performed simulation runs for several different BSFs between 0.1 and 1.0, which are summarised in Fig. 2. For values up to 0.66 an almost linear dependence can be observed. Beyond this point, the thermal expansion was found to decrease again; however, simulations with larger BSF values were not reproducible, which is reflected in larger error bars. The experimental value is matched best for \( \eta = 0.2 \).

![Fig. 1 Calculated average bond lengths in GaAs for different BSFs. Linear fits were obtained between 200 and 500 K from five independent simulation runs for each BSF and temperature. Compared with scaling factors of 0.2 and 0.5, a value of 1.0 leads to increased spread in data points.](image)

Fig. 1

![Fig. 2 Thermal expansion coefficients against BSF for GaAs. Experimental value is best matched for scaling factor of 0.2. For scaling factors above 0.66, thermal expansion coefficient decreases again, in combination with increased error.](image)

Fig. 2

![Fig. 3 Thermal expansion coefficients for different simulation box sizes, modelled with \( \eta = 0.2 \). Calculated values are shown to be robust with respect to total number of atoms. Error bars of almost constant magnitude indicate that error is inherent to method and also does not depend on number of atoms.](image)

Fig. 3

Intuitively, the scaling factor of 0.2 can be justified by the fact that one random move potentially increases the energy of five atoms. A reduction of the acceptance probability by a factor of five therefore

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**ELECTRONICS LETTERS 3rd September 2015 Vol. 51 No. 18 pp. 1455–1457**
yields in a more realistic reproduction of the thermal expansion in III–V materials.

This modification to the MMC algorithm was also tested for robustness with respect to the simulation box size. The corresponding data for simulation box edge lengths between 2 and 7 unit cells are composed in Fig. 3 for GaAs and InAs. The thermal expansion coefficient is still overestimated slightly, although the error is almost constant for different sizes.

Comparison for different III–V materials: This method was applied to atomistic models of the most common III–V compounds in a zincblende lattice. Corresponding data are compiled in Fig. 4 and Table 1. Simulations, performed with the classic MMC algorithm, i.e. with \( \eta = 1.0 \), were found to be comparable with the values in [8]. All obtained data points clearly indicate a significant improvement compared with previously published data.

![Fig. 4 Calculated thermal expansion coefficients summarised for different binary III–V materials. Data points obtained with BSF of 0.2 led to errors of \( \sim 10\% \), with exception of GaSb. Data point for GaAs is matched even better with error of 3%. Reference data are taken from [15, 16, 8].](image)

**Table 1: Calculated thermal expansion coefficients compared with experimental data and previously published modelling works [8].** Relative errors for calculated values are given in brackets.

| Material | Experimental (1/K) | Rathi et al. (1/K) | This work (1/K) |
|----------|-------------------|-------------------|----------------|
| GaAs     | \( 5.73 \times 10^{-6} \) | \( 1.25 \times 10^{-6} \) (118.2%) | \( 5.89 \times 10^{-6} \) (2.8%) |
| InP      | \( 4.6 \times 10^{-6} \) | \( 9.66 \times 10^{-7} \) (110.0%) | \( 5.10 \times 10^{-7} \) (10.9%) |
| InAs     | \( 4.52 \times 10^{-6} \) | \( 9.29 \times 10^{-7} \) (105.5%) | \( 5.01 \times 10^{-7} \) (10.8%) |
| GaSb     | \( 6.1 \times 10^{-6} \) | \( 1.06 \times 10^{-6} \) (73.8%) | \( 5.04 \times 10^{-7} \) (−17.4%) |
| InSb     | \( 5.37 \times 10^{-6} \) | \( 1.10 \times 10^{-6} \) (104.8%) | \( 4.76 \times 10^{-7} \) (−11.4%) |

With the exception of GaSb, all calculated values were found to be around the 10% band of the experimental value. Errors of similar magnitude, which were also obtained in an analysis of the elastic behaviour, are to be expected due to the simplified nature of the Tersoff potential [10].

**Conclusion:** This Letter provides a method to allow atomistic models of III–V materials at elevated temperatures yielding accurate values for the thermal expansion coefficient and therefore resulting thermal strain. Compared with previous works, the error could be reduced from more than 200% to around 10% for most III–V materials. The MMC acceptance criterion for random moves with a positive energy balance is modified by an additional factor, which both suppresses exceeding thermal expansion and leads to clearly reduced statistical errors. This enables the simulation of thermal strain as well as diffusion or growth processes, which typically takes place at several hundred K, under realistic conditions.

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