Empirical interatomic potential for the mechanical, vibrational and thermodynamic properties of semiconductors

U Monteverde¹, M A Migliorato¹ and D Powell²

¹ School of Electrical and Electronic Engineering, University of Manchester, Sackville Street Building, M13 9PL, Manchester, UK

² Intercollege Larnaca, 52 Famagusta Avenue, Larnaca-Dhekelia Road, Larnaca, 6019, Cyprus

Abstract. Empirical models are widely used to simulate large atomic structures where instead ab initio methods are not practical because of computational limitations. However models such as Tersoff potential [8], [9], Valence Force Field [13], [14] or Stillinger-Weber potential [15] have some restrictions in correctly predicting simultaneously both elastic and vibrational properties of the crystals [18]. Thus, extension of the functional form of the potentials by including further atomic interactions [20] [21] compared to the simple 2- and 3-body terms, is required. An empirical interatomic potential is proposed which represents a substantial improvement of the Tersoff potential for semiconductors modelling. The new model includes multi-bond interactions and the volume dependency by considering the tetrahedron distortions of the covalent crystal.

1. Introduction

Strain in a semiconductor changes the electronic properties hence the intrinsic stress in an heterostructure has a direct influence on device behavior [1]-[4]. In device design it is of fundamental importance to understand the relation between the strained crystalline structure and the vibrational properties [5], [6] of the material [7].

Many computational methods have been introduced to simulate crystal properties. Based on the first-principles quantum mechanics Density-Functional Theory (DFT) gives accurate descriptions but with high computational effort the size of system under simulation is limited. An easier approach is given by the tight-binding approximation, which leads to a semi-empirical method that still requires high computation. A third way to describe physical feature of a solid is by empirical potentials [8]-[15]. The great advantage of empirical methods is on the reduced calculation effort but the number of simulated properties can be limited by the functional form of the potential itself or it depends on the parameterization.

2. Conventional Tersoff potential

Based on the Morse-type potential, Abell [16] showed that the binding energy of a system can be described by considering a simple atomic pair interaction independently from the local environment. This pair potential model was further extended by multiple atomic interactions: two- and three-body terms were included in the Stillinger-Weber potential [15] as well as in the Tersoff potential. The
general concept introduced by the latter model was that the tendency of two atoms to hold a bond is obstructed by their nearest atoms which exert an angular force on the bond.

The Tersoff potential, rearranged later by Smith [17], has the form:

\[ V_{ij} = f_c(r_{ij}) \left[ V_R(r_{ij}) - b_{ij}V_A(r_{ij}) \right] \] (1)

\[ V_R(r_{ij}) = \frac{D e^{-\beta \sqrt{2S} \left( r_{ij} - R_e \right)}}{S - 1} \] (2)

\[ V_A(r_{ij}) = \frac{SD e^{-\beta \sqrt{2S} \left( r_{ij} - R_e \right)}}{S - 1} \] (3)

where \( r_{ij} \) is the distance between the bonded atoms \( i \) and \( j \), \( V_R(r_{ij}) \) and \( V_A(r_{ij}) \) are the repulsive and attractive potentials of the pair \( i-j \) respectively; \( f_c(r_{ij}) \) is a cut off function and \( b_{ij} \) is the bond-order which introduces a dependence on the local environment given by:

\[ b_{ij} = \left[ 1 + \left( \xi_{ij} \right)^n \right]^{-1/n(2n)} \] (4)

\[ \xi_{ij} = \sum_{k \neq i,j} f_c(r_{ik}) g(\theta_{ijk}) e^{\lambda (r_{ij} - r_k)} \] (5)

\[ g(\theta_{ijk}) = 1 + \left( \frac{C}{D} \right)^2 - \frac{C^2}{D^2 + (H - \cos(\theta_{ijk}))^2} \] (6)

\( f_c(r_{ik}) \) is again a cut off function and \( g(\theta_{ijk}) \) is a function of the bond angle. The model has 10 degrees of freedom as much as the number of parameters (\( D_e, S, R_e, \beta, \gamma, n, \lambda, D, C, H \)) that need be fitted to properly describe the bonding strength and the behaviour of the material. In Table 1 we show the mechanical properties of Silicon simulated with the Tersoff potential along with the phonon dispersion curves in Figure 1 using a parameterization from [22].

![Figure 1. Phonon dispersion curves of Silicon calculated with the conventional Tersoff potential (solid lines) [22] and experimentally measured (circles) [23].](image-url)
The inconsistency of the potential in predicting at the same time the mechanical properties (Table 1) and the dispersion curves (Figure 1) is evident. The excellent estimation of the elastic constants is achieved at the expense of the phonon frequencies. The limit of the model was in part pointed out by Tersoff in his earlier publications, where the phonons overestimation was attributed to a common feature of the short-ranged models [8], [18], [19].

### 3. New potential

We introduced in the conventional potential model two secondary forces: a repulsive force $V_{R}(r_{ij})$ and an attractive force $V_{A}(r_{ij}, r_{ik})$. These forces are modulated by a 4-body term $a_{jk}$ and a 3-body term $c_{jk}$, and their contribution rises when the tetrahedron is out of equilibrium. Thus, the expression of the new potential becomes:

$$V_{ij} = f_{i}(r_{ij})\left[V_{R}(r_{ij}) + a_{jk}V_{R}(r_{jk}) - b_{ij}V_{A}(r_{ij}) - c_{jk}V_{A}(r_{jk})\right]$$  \hspace{1cm} (7)

$$V_{R}(r_{ij}) = B_{i}e^{-\rho(r_{ij}-R_{ij})}$$  \hspace{1cm} (8)

$$V_{A}(r_{ij}, r_{ik}) = U_{ij}e^{-\sigma\left|\sum_{k}r_{ik}\right|}$$  \hspace{1cm} (9)

where the terms in tilde indicate that respect to their definitions in the Tersoff model some modifications have been introduced. The attempt here is to give to the potential a dependency upon the volume distortion and a multi-bond interaction through the terms:

$$a_{jk} = \left[1 - \frac{1}{3} \sum_{k \neq j} e^{W_{(\cos\theta_{ijk}-\cos\theta_{ijk})}(\cos\theta_{ijk}-\cos\theta_{ijk})}\right]^{2}$$  \hspace{1cm} (10)

$$c_{jk} = \left[1 - \frac{1}{3} \sum_{k \neq j} e^{W_{(\cos\theta_{ijk}-\cos\theta_{ijk})}(\cos\theta_{ijk}-\cos\theta_{ijk})}\right]$$  \hspace{1cm} (11)

where $j$, $k$, $k''$ and $k'''$ are neighbours of the central atom $i$ and the summation is over $k$ because the atomic distances are all defined once the edge $jk$ of the tetrahedron is considered. The term $a_{jk}$ is a significant term of the new model as much as the bond-order term $b_{ij}$ of the classic potential. In $b_{ij}$ two
competing bonds \((ij, ik)\) are considered through the angle \(\theta_{ijk}\) and the difference \(r_{ij} - r_{ik}\), whereas in \(a_{jk}\) the couple of bonds \(ij\)-\(ik\) compete in stretching and torsion with the opposite couple \(ik''-ik'''\) through the distances between bonds. The term \(c_{jk}\), given in equation 11, plays a more effective role in the adjustment of the dispersion curves out the high symmetry points and in the Grüneisen parameters by taking into account the tetrahedron distortion through the angles of its faces \(\theta_{jk''}\) and \(\theta_{jk'''}\) having the same edge \(jk\).

Compared to the original potential we have also introduced in \(\zeta_{ij}\) a term depending on the angle between two faces of the tetrahedron \(\theta_{jk''}, \theta_{jk'''}\) and rewrote the angular function \(g(\theta_{jk})\) as a series of cosines which converges very rapidly to the equilibrium bond angle:

\[
\zeta_{ij} = \sum_{k \neq j} f_k (r_{jk}) g_k^2 (\theta_{jk}, \lambda) (r_{jk} - r_{jk''}) (\cos \theta_{jk''} - \cos \theta_{jk'})
\]

(12)

\[
\hat{g}(\theta_{jk}) = H + C \cos(\theta_{jk}) + D \cos(2\theta_{jk}) + E \cos(3\theta_{jk}) + F \cos(4\theta_{jk})
\]

(13)

Figure 2. Phonon dispersion curves of Silicon calculated with the modified Tersoff potential (solid lines) and experimentally measured (circles) [23].

| Property       | Measured | Simulated |
|----------------|----------|-----------|
| \(E_{\text{coh}}\) (eV)  | -4.63    | -4.64806  |
| Lattice C. (\AA)   | 5.431    | 5.39575   |
| B (Mbar)          | 0.9783   | 0.946459  |
| C' (Mbar)         | 0.509    | 0.509235  |
| \(C_{11}\) (Mbar) | 1.657    | 1.62544   |
| \(C_{12}\) (Mbar) | 0.639    | 0.60696   |
| \(C_{44}\) (Mbar) | 0.796    | 0.79601   |

Table 2. Mechanical properties of Silicon calculated with the modified Tersoff potential.

| Property       | Measured | Simulated |
|----------------|----------|-----------|
| \(\Gamma_{\text{LO, TO}}\) | 0.98     | 1.28      |
| \(X_{\text{TA}}\)         | -1.40    | -1.80     |
| \(X_{\text{LA, LO}}\)     | 0.90     | 1.23      |
| \(X_{\text{TO}}\)         | 1.50     | 1.64      |
| \(L_{\text{TA}}\)         | -1.30    | -1.45     |
| \(L_{\text{TO}}\)         | -1.30    | -1.43     |

Table 3. Grüneisen parameters of Silicon calculated with the modified Tersoff potential.
The potential model has now 11 more degrees of freedom (due to the new parameters: $B_e$, $U_e$, $P_e$, $\rho$, $\sigma$, $L$, $\eta$, $W$, $v$, $E$, $F$) which allow as to fit mechanical properties, phonon dispersion curves and Grüneisen parameters. The results of a simulation on Silicon with the described new potential are listed in table 2 and table 3, and the phonon dispersion curves are shown in figure 2; all simulations and parameterizations were performed on a Desktop PC using in-house software initially developed by Dr. D. Powell and Dr. M. A. Migliorato.

The phonon frequencies predicted (figure 2) at the high symmetry points, particularly for the acoustic modes, are in good agreement with the experimental data and the calculated elastic constants (table 2) are in excellent agreement compared with others empirical potentials [11] [21]. Moreover, another important result lies in the good estimation of the Grüneisen parameters (table 3), since all empirical models known fail in such estimation, mainly in the prediction of the negative values.

4. Conclusion

The model presented is able to simultaneously predict the elastic constants and phonon dispersion curves of the materials along with the Grüneisen parameters which are directly linked to the thermodynamic properties of the system under investigation. Instead, the flattening of the phonon transverse acoustic branches is poorly reproduced due to the absence in the model of the long-range atomic interactions. Although the number of parameters required by the model to fit the semiconductor’s properties was increased, the computational effort was not altered since the terms introduced depend on the first nearest neighbours only.

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