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Modelling of the phonon strain shift coefficients in $\text{Si}_{1-x}\text{Ge}_x$ alloys

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Abstract. In the Raman spectrum of epitaxial $\text{Si}_{1-x}\text{Ge}_x$ alloys, the composition effect, that determines the three mode peak position, is superimposed to the phonon shift caused by strain. Therefore, the experimental spectra interpretation remains not straightforward, unless vibrational properties calculations of such systems are available. In this paper, reticular dynamic calculations within a modified Keating model, the Anharmonic Keating, are discussed. A new set of model parameters is introduced, providing simple and predictive supercell calculations to investigate accurately the three Raman-active phonon modes in $\text{Si}_{1-x}\text{Ge}_x$ alloys. The recalculated AK model is successfully employed to model the zone centre Raman-active phonon modes of relaxed and hydrostatically stressed $\text{Si}_{1-x}\text{Ge}_x$ alloys. The results of the calculations are in quantitative agreement with experimental data reported in literature.

1. Introduction

Nowadays, $\text{Si}_{1-x}\text{Ge}_x$ /Si heterostructures are emerging systems because of the high potential to improve performances of standard Si devices: $\text{Si}_{1-x}\text{Ge}_x$ alloys allow band gap and strain engineering, retaining the well-established Si technology. Raman spectroscopy has already been demonstrated to be an effective technique to evaluate strain in Si-based microelectronic devices, since lattice vibrations depend on this parameter. In an epitaxial $\text{Si}_{1-x}\text{Ge}_x$ alloy, however, Ge-Ge, Si-Ge and Si-Si nearest neighbours vibrations are present and strain and composition contributions affect similarly the three mode peak positions. As a consequence, the information regarding these two parameters is not obviously available from the Raman experiments. Different approaches to the lattice dynamics of $\text{Si}_{1-x}\text{Ge}_x$ alloys have been therefore developed [1, 2, 3, 4, 5], because a detailed comparison of the model calculation results with the experimental Raman measurements, can allow to explain spectra features: assigning the correct vibrational modes [6], or allowing to predict the modifications in the experimental spectra, induced by perturbations such as hydrostatic pressure [7].

In the present work, a theoretical approach to the lattice dynamics of $\text{Si}_{1-x}\text{Ge}_x$ alloys within a Valence Force Field framework is discussed. We employed a modified Keating model: the Anharmonic Keating (AK)[5], to perform supercell calculations. AK model calculations have already explained successfully the microscopic origin of the phonon spectra details of relaxed $\text{Si}_{1-x}\text{Ge}_x$ alloys, including phonon modes dependence on the possible atom configurations [5, 6]. However, in the following discussion, it will be shown that a new set of force constants must be introduced, in order to get an accurate description of the phonon frequencies of $\text{Si}_{1-x}\text{Ge}_x$ alloys.

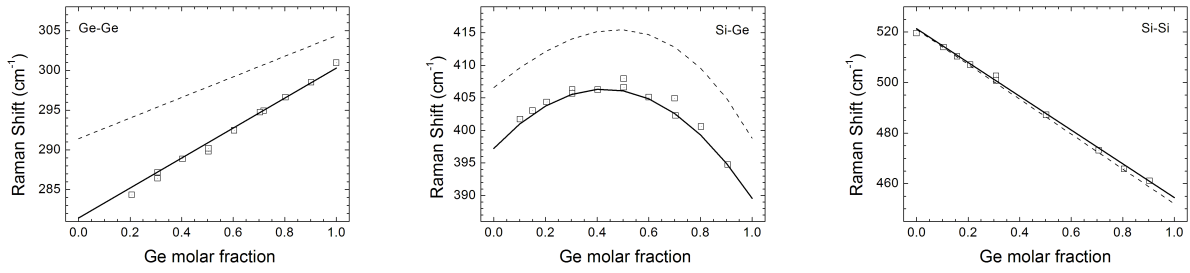


Figure 1. Three main Raman mode frequencies of $\text{Si}_{1-x}\text{Ge}_x$ alloys as a function of the Ge content. Open symbols are data from Ref [9], while dashed and solid lines are calculation results according, respectively, to parameters of Ref. [5] and of table 1.

2. Results

Keating's two-parameter model [8] describes the dynamics of diamond lattices using the following strain energy, E :

$$E = \sum_{i,j} \frac{\alpha}{a_0^2} (\Delta(r_{ij}^2))^2 + \sum_{i,j,k \neq j} \frac{\beta}{a_0^2} (\Delta(\vec{r}_{ij} \cdot \vec{r}_{ik}))^2 \quad (1)$$

where a_0 is the equilibrium lattice constant, \vec{r}_{ij} is the bond length between lattice sites i and j and $\Delta(\vec{r}_{ij} \cdot \vec{r}_{ik}) = \vec{r}_{ij} \cdot \vec{r}_{ik} - \vec{r}_{ij}^0 \cdot \vec{r}_{ik}^0$, where the 0 index is relative to the perfect diamond lattice. The elastic energy due to changes in bond lengths is given by α , while β describes a bond-bending force constant. These parameters depend on the atomic species of the corresponding bond. The Keating model has been used to study static and elastic properties of covalent semiconductors. However, since the force constants account only for the short range part of the electrostatic force, the phonon dispersion curves, calculated in this framework, give a wrong prediction of the zone-edge transversal acoustic (TA) phonons [10]. The Keating model cannot even describe properly $\text{Si}_{1-x}\text{Ge}_x$, because of the local distortion which accompanies the alloying, due to the different atomic size of Si and Ge atoms. Thus, higher order terms must be included in the strain energy (Eq. 1) for a realistic description of large lattice deformations. Using force constants, which depend explicitly on the local geometry, Rücker and Methfessel, modified the Keating model in order to include anharmonic effects, simply by scaling the force constants α and β with respect to bond length and bond angle, θ [5]: $\alpha = \alpha(\alpha_0, \vec{r}_{ij})$ and $\beta = \beta(\beta_0, \nu, \vec{r}_{ij}, \vec{r}_{ik}, \theta)$. Here, ν is a scaling exponent nearly independent on the material and α_0 and β_0 are the anharmonic force constants. We employed this AK model to perform supercell calculations. The cubic supercell consists of about 4000 atoms with lattice sites randomly occupied by Si and Ge, according to the desired composition. The unit cell is refined adjusting its shape and the atoms coordinates to minimise the AK potential energy. The eigenfrequencies are then obtained by direct diagonalization of the dynamical matrix, as described in Ref. [5].

In Fig. 1, the frequency of the three optical modes of the relaxed alloys, calculated using the parameters of table VI in Ref. [5], are reported as a function of the Ge molar fraction. Although the calculated frequency of the Si-Si mode nicely follows the measured Raman shift of bulk materials [9], the model results badly fail to predict both Si-Ge and Ge-Ge mode composition dependence. These discrepancies can be explained and solved via the following considerations. A comparison with the available experimental literature data [11] shows that the AK force constants in Ref. [5] were tuned to reproduce the zone centre optical phonon frequency at room temperature (RT) for Si, but at low temperature (LT) for Ge. The anharmonic model, however, gives a correct prediction of the pure Ge experimental Grüneisen parameter [5], which roughly relates the thermal expansion with the Raman mode shift. As a consequence, it can be expected

Table 1. Anharmonic Keating force constants, in atomic units, after [5] for Si, while Ge and SiGe data have been obtained in this work.

	α_0	β_0
Si	0.0580	0.0140
Ge	0.0475	0.0147
SiGe	0.0511	0.0139

that a more accurate reproduction of the Raman-active phonons, commonly measured at RT, could be obtained by means of a direct recalculation of the corresponding Ge and SiGe Keating force constants. The new Keating parameters have been introduced via the following procedure. The Keating parameters α and β are related to some macroscopic bulk properties through the following equations [5]:

$$C_{11} - C_{12} = \frac{4}{a_0}\beta, \quad C_{44} = \frac{4}{a_0} \frac{\alpha\beta}{\alpha + \beta}, \quad (2)$$

$$B = \frac{1}{a_0} \left(\alpha + \frac{1}{3}\beta \right), \quad m\omega_0 = 8(\alpha + \beta). \quad (3)$$

Here a_0 is the relaxed lattice parameter; m , the reduced mass; C_{ii} , with $i=1,2,4$, the elastic constants; B , the bulk modulus; ω_0 the zone centre optical phonon frequency. As a first step, these equations have been employed with the Ge RT data [12], to get the α_0^{Ge} and β_0^{Ge} *ansatz*. But, in a $\text{Si}_{1-x}\text{Ge}_x$ alloy an accurate description of the Ge-Ge vibration confinement to the subspace of Ge-Ge bonds, cannot be obtained only by means of the reproduction of the zone centre optical phonon in the pure element. In fact, the relaxation of the momentum conservation, due to the chemical disorder, allows forbidden modes with large k -vector to be involved in the first order Raman spectrum. We therefore compared the calculated Ge RT phonon dispersion curves with the available experimental data [11, 13, 14, 15] (figure 2). According to the described above limits of the model in the acoustic region, an appropriate reproduction of the RT optical modes has been obtained. This should be the purpose of a model well-suited to predict experimental Raman spectra in common set-ups, i.e. in a back-scattering geometry from the (001) surface of a diamond type crystal, since only the longitudinal optical mode is Raman-active. Finally, we recalculated the α_0^{Si-Ge} and β_0^{Si-Ge} force constants to reproduce the experimental Si-Ge optical phonon frequency for a $\text{Si}_{0.5}\text{Ge}_{0.5}$ bulk crystal [9]. The resultant Ge and SiGe Keating parameters obtained in this work are given in table 1.

The shifts of the Raman peaks as a function of the relaxed alloy composition, given by the recalculated AK model are thus summarised in Fig. 1 as solid lines. Now, for each vibrational mode there is a good quantitative agreement with the measured data on bulk samples [9], over the whole composition range. The recalculated AK model is therefore expected to be an appropriate tool to investigate also the shift of Raman modes due to macroscopic external stress. To address this effect, the recalculated AK model has been employed to predict Raman spectra of $\text{Si}_{1-x}\text{Ge}_x$ alloys under hydrostatic strain. For a desired Ge composition, we fixed the lattice parameter in order to fulfil a given pressure. The Raman spectra for different stress conditions were calculated as described previously. The linear coefficient $d\omega^i/dp$, for each i -mode, was determined by a second order polynomial fit of the phonon mode ω^i as a function of the pressure p . Beside a well reproduction of the pure material experimental data, as shown in Fig. 3, the refitted AK model gives also a nice description of the $d\omega^i/dp$ dependence on composition, Ref. [7].

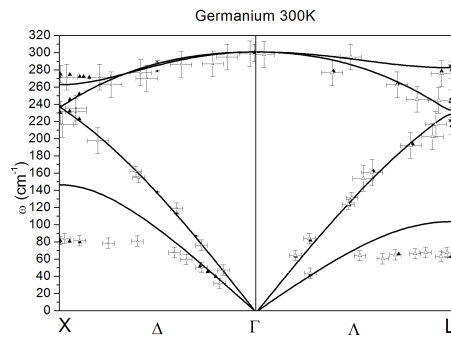


Figure 2. Ge phonon dispersion curves at room temperature. Solid lines are recalculated AK model results, while symbols are the experimental data of Ref. [11, 13, 14, 15]

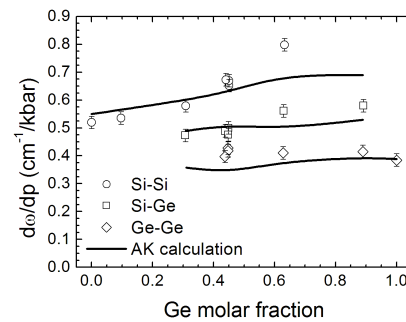


Figure 3. Dependence of the $d\omega^i/dp$ coefficient on the Ge molar fraction for the three Raman modes of hydrostatically strained alloys. Open symbols are data from Ref.[7], while solid lines are the AK model results.

3. Conclusion

In conclusion, the Anharmonic Keating model was used to study the Raman-active optical phonon frequencies in $\text{Si}_{1-x}\text{Ge}_x$ alloys. A theoretical approach to the lattice dynamics of strained $\text{Si}_{1-x}\text{Ge}_x$ alloys is necessary in order to easily decouple the composition and strain contributions. A new set of Keating parameters has been introduced to describe quantitatively phonon frequencies of relaxed $\text{Si}_{1-x}\text{Ge}_x$ alloys. Moreover, we have shown that the recalculated model predicts the Raman-active phonon strain shifts induced by hydrostatic pressure in $\text{Si}_{1-x}\text{Ge}_x$ alloys. This study suggests the recalculated AK model could be effective to investigate the effect of the biaxial strain on Raman-active modes of $\text{Si}_{1-x}\text{Ge}_x$ alloys epitaxially grown on Si substrates.

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