LATTICE PROPERTIES OF Ge AND GaAs STRAINED-LAYERS ON Si

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ABSTRACT

A phenomenological lattice dynamics model has been developed that describes how strain affects phonon frequencies and elastic constants in Group IV and III-V semiconductor thin films and strained layers. Using this model, the phonon dispersion relations for strained-layer heterostructures of Ge and GaAs on Si have been obtained in the quasiharmonic approximation. This model uses available experimental data and can predict the effect of arbitrary strains on thin films.

INTRODUCTION

The symmetry of a crystal can be altered by the presence of strains. This strain can also lift phonon degeneracies, and induce upward or downward shifts of the frequencies that are linear in strain to first order. The strains can be either induced by external stresses, or due to growth conditions or modifications of the materials (built-in). Built-in strains in epilayers and superlattices are produced by lattice mismatch or by the different thermal expansion coefficients of the material layers involved. Considerable effort has been spent to understand the electronic and phonon properties of strained-layer superlattices, which depend critically on the effects of biaxial strain [1-3]. The folding of acoustic phonons and the confinement of optical phonons in superlattices can give rise to many $k \approx 0$ zone center phonons that are IR and/or Raman active, depending on the superperiodicity. The measurement of strain-modified phonon frequencies can be used as a diagnostic tool to examine the structure of the thin film.

Cerdeira *et al.* introduced the microscopic p, q, and r parameters to account for the strain-shift and splitting of the zone center phonon frequencies [4]. They evaluated these parameters by using a Keating and valence force field model and assumed that the splitting between zone center TO and LO modes in heteropolar semiconductors is independent of strain. Later, Anastassakis *et al.* introduced effective charge deformation potentials to account for the different strain shift of these modes [5]. Talwar and Vandevyver used an 11 parameter rigid ion model to study the effects of pressure on the vibrational properties of Ga-In pnictides [2]. While their one phonon and two phonon densities of states, Debye temperatures, Gruneisen constants, and linear thermal expansion coefficients were all in reasonably good agreement with existing experimental data, this model showed the flatness of the lowest TA branches at ambient pressure but not at elevated pressures. This raised the question of whether the bending of the TA branch under compression was an artifact of the rigid ion model or was due to the peculiarity of compound semiconductors. Weinstein *et al.* suggested use of the bond charge model (BCM) to study the pressure dependence of phonon dispersion relations [1]. Mayer and Wehner tried to extend the BCM to account for the strain-dependent phonon properties of Si by including third order anharmonic

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potentials [6]. The mode Gruneisen parameters they obtained were not in good agreement with available experimental values. They suggested that the problem was in the harmonic part of the potentials and then modified the BCM by including shell interactions similar to those in the Shell Model [7]. This new model with eight harmonic and five anharmonic parameters produced reasonable agreement with experimental results. Sui and Herman used a modified Keating/valence force field model with strain-dependent force constants to study stress dependent phonon properties of Group IV semiconductors and strained-layers of these materials [3]. The mode Gruneisen parameters they obtained were in good agreement with experimental data.

In this work, the effects of strain on the phonon dispersion of diamond and zincblende cubic crystals are investigated by using a bond-charge model. Emphasis is placed on bulk Ge and GaAs and their strained-epilayers and superlattices.

BOND-CHARGE MODEL AND THE QUASIHARMONIC APPROXIMATION

One important characteristic of the phonon dispersion of diamond and zincblende crystals is that the TA branch phonons have very low frequency and the TA branches are very flat away from the zone center. The Weber bond charge model is by far the most successful phenomenological model in producing these features, and it uses fewer parameters than do other models (six and four parameters for zinc-blende and diamond structure materials, respectively) [8, 9]. In this model, adiabatically moving bond charges (BC) are introduced on the bonds to mimic the charge distribution of the crystal, allowing one to treat electron mediated ion-ion forces in a simple way. Metal-like and covalent bonding are represented by short-range central forces between ions and by interactions involving the BCs, respectively. For homopolar semiconductors the BCs are in the middle of the bond, whereas for III-V semiconductors they are nearer to the cations. The BCM interactions are: **(a)** nearest neighbor ion-ion central potential $\Phi_{\text{i-i}}$, **(b)** nearest neighbor central ion-BC potential $\Phi_{\text{i-bc}}$, **(c)** Keating bond-bond interaction V_{bb}, and **(d)** Coulomb interaction between ion-ion, BC-BC, and ion-BC.

In the *quasiharmonic approximation,* the changes in the force constants are obtained as follows: the central ion-ion and ion-BC interactions are supposed to scale with the change in the distance between the two "particles" (i.e., ions or BCs). The Keating bond-bending term scales with the change in the angle between the particles. These interactions scale, respectively, as:

$$\Phi''_{i-i}(\varepsilon)=\Phi''_{i-i}(0)\left[1+m_{i-i}\frac{\Delta r}{r}\right] \tag{1}$$

$$\beta_{ij}(\varepsilon)=\beta_{ij}(0)\left[1+m_{\beta}\frac{\Delta r}{r_{ij}}+l_{\beta}\frac{\Delta(\cos(\theta_{ij}))}{\cos(\theta^{0}_{ij})}\right] \tag{2}$$

$\cos(\theta^{0}_{ij})=-1/3$ is the equilibrium bond angle (no strain) between bonds i and j.

Under an arbitrary strain, the bond lengths and angles change as:

$$\Delta r = \vec{r} \cdot \Delta\tilde{u} \tag{3}$$

$$\Delta\theta_{ij} = \frac{1}{2a}\left(r_i \cdot \Delta\tilde{u}_j + r_j \cdot \Delta\tilde{u}_i\right) \tag{4}$$

where Δu is the static plus dynamic displacement:

$$\Delta\tilde{u} = \frac{\vec{\varepsilon}.\vec{r}}{a} - a\varsigma\left[\varepsilon_{yz}, \varepsilon_{xz}, \varepsilon_{xy}\right]^T + \Delta u_d \tag{5}$$

ε is the strain tensor, r_i is the i^{th} bond vector, ξ is the internal strain parameter, a is lattice constant divided by four and T stands for transpose.

Hydrostatic Pressure

When the crystal is subjected to hydrostatic pressure, the strain is diagonal and is given by $\varepsilon_h = -P/3B$; P is the applied pressure and B is the bulk modulus. In the case of a strain induced by a hydrostatic pressure, the symmetry of the crystal is not lowered and consequently the bond angles do not change; bond lengths change by $\Delta r = r_0\varepsilon_{xx}$. The force constants are modified according to Equations 3 and 4. The Coulomb contribution to the force constants is obtained by Ewald summation for the strained crystal.

The mode Gruneisen parameter is defined as: $\gamma_i = -d\ln\omega_i / d\ln V = -\Delta\omega_i / (3\varepsilon_h\omega_i)$, where V is the volume of the crystal. γ_i at the Γ, X and L points of the Brilluion Zone [1] are used to fit the strain parameters for the harmonic force constants m_{i-i} (interaction a), m_{i-bc} (interaction b) , m_β (interaction c) and m_z (interaction d). For Ge, m_{i-i}, $-m_{i-bc}$ and m_z are almost equal to each other ($m_{i-i} \approx 12.5$). m_β is very small (≈1.7), as is expected since the Keating interaction is dependent on the bond angles and hydrostatic pressure preserves the angle between the bonds.

For III-V materials this procedure is not easy to implement because of long-range Coulombic interactions. It is assumed that each force constant has a similar functional dependence on strain and that the positions of the bond charges are dependent on the strain. The macroscopic electric field and the new equilibrium first potential derivatives were calculated and mode Gruenisen parameters were fitted to the experimental values [1] at the Γ, L, X, and K points.

In Figure 1 the dispersion in GaAs and Ge mode Gruenisen parameters are plotted along the Γ-Δ-X-K-Γ-L directions. Also, contrary to the results of Ref. 2, no substantial change in the shape of the TA branches with pressure is found.

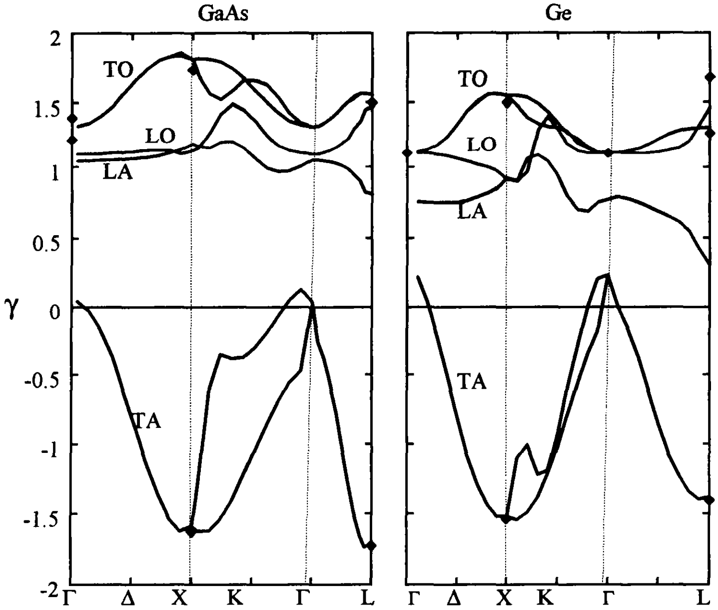

Figure 1. The mode Gruneisen parameters for GaAs and Ge. Experimental data points are from Ref. 1.

Biaxial Strains

Biaxial Strain in the (001) plane

Uniaxial stress in the (001) direction can arise during pseudomorphic growth of a thin film on a (001) substrate with a different lattice constant. The strain tensor can be decomposed into a hydrostatic part $\varepsilon_h = 2(1 - C_{12}/C_{11})\varepsilon_{xx}/3$ and a shear part $\varepsilon_s = -(1 + 2C_{12}/C_{11})\varepsilon_{xx}/3$, where $\varepsilon_{xx} = (a_s - a_f)/a_f$, and a_s, a_f are lattice constants for the substrate and film respectively.

The hydrostatic part affects only the bond length and the shear part affects only the bond angles. Bond angle changes are given in Ref. 3. In homopolar materials, zone center optical phonon frequencies split into a singlet and a doublet. In heteropolar materials, the degeneracy of the TO mode is lifted.

Biaxial Strain in the (111) Plane

When biaxial strain is in the (111) plane, in addition to the macroscopic strain, an internal strain parameter ξ is needed to uniquely define the relative position of the atoms; this gives the relative displacements of the two face centered cubic lattices of the diamond structure.

The elements of the strain tensor are:

$$\varepsilon_d = \frac{2C_{44}}{2C_{44} + C_{11} + 2C_{12}} \varepsilon_{\parallel} \tag{6}$$

$$\varepsilon_o = \frac{(C_{11} + 2C_{12})}{2C_{44} + C_{11} + 2C_{12}} \varepsilon_{\parallel} \tag{7}$$

where ε_d and ε_o are the hydrostatic and shear components, and the C's are the second-order elastic constants.

There are two different bond length and bond angle changes for this strain configuration, as was seen in Ref. 3. The splittings at the Γ point are similar to those in the (001) case.

The frequency splitting for (001) strain at the Γ point is needed to determine the strain coefficient of the β term in Equation 2, and the (111) splitting is used to check this value. In Figure 2, phonon frequency shifts for Ge lattice matched to Si on (001) are plotted with these strain-modified force constants.

SUMMARY

The bond charge model has been modified to study the strain dependence of phonon frequencies of diamond and zinc-blende type semiconductors. Calculated mode Gruneisen parameters are in good agreement with experimental values. For Ge, only two parameters are needed in this calculation. Under hydrostatic pressure, bond charges move towards the center of the bonds for the III-V materials, as is expected [9]. Details of this work, including application to other Group III-V and to II-VI semiconductors and an investigation of the strain dependence of the elastic constants will be published elsewhere.

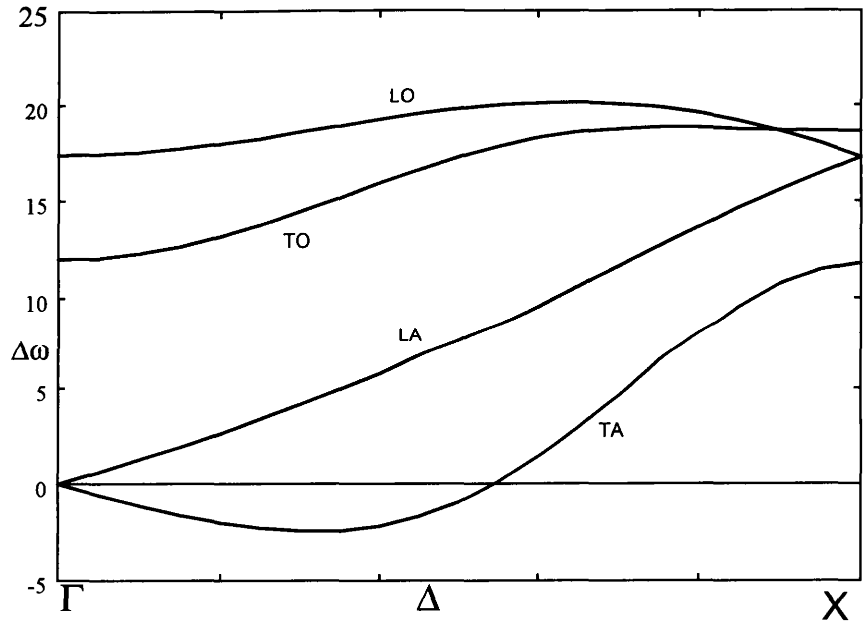

Figure 2. The phonon frequency shift Δω (cm^{-1}) along the growth direction for Ge pseudomorphically grown on Si (100).

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