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FIRST PRINCIPLES CALCULATIONS OF INTERFACE PHONONS OF AN EPITAXIAL Sb MONOLAYER ON GaAs(110) AND InP(110)

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Vibrations of an epitaxial layer of Sb on the (110) surface of GaAs and InP have been investigated using *first principles* pseudopotential calculations. The Hellmann-Feynman forces were employed to calculate the dynamical matrix at the $\bar{\Gamma}$-point. The resulting eigenvalues and eigenmodes are discussed in the context of recent Raman scattering experiments and tight-binding results.

In the recent past a great deal of work, experimental as well as theoretical, has been published on the atomic and electronic structure of an ordered monolayer growth of Sb on III-V(110) surfaces. However, relatively fewer studies of interface phonons have been reported. By analysing the results of Raman scattering measurements carried out for an ordered monolayer (1ML) Sb covered (110) surfaces of InP, GaAs, and GaP Hünerman[1] and Hünermann *et al* [2] have observed interface phonons. These phonon modes correspond to vibrations involving the epitaxial layer of Sb and the upper substrate layer. For Sb/InP(110) these authors have reported 8 pronounced peaks which fulfill the polarization selection rules for the Sb chain along the $[\bar{1}10]$ direction. Godin *et al* [3] have used a tight-binding total-energy model to generate via the Hellmann-Feynman forces the dynamical matrix for the overlayer atoms only. Employing this restricted dynamical model they find 4 optical eigenmodes and eigenfrequencies of the Sb chain on GaAs(110). Their results are claimed to be in reasonable agreement to experimental results[4]. However, in our view a full agreement between experiment and theory is missing. In this work we report on a *first-principles* calculation of interface phonon modes of an epitaxial Sb monolayer on GaAs(110) and InP(110).

Our calculations are based on the density-functional theory (DFT)[5,6]. The electron-ion interaction is treated by using norm-conserving, *ab initio*, fully separable pseudopotentials[7] as given in Stumpf *et al* [8] and the many-body electron-electron interaction is treated within the local-density approximation (LDA) and the Ceperley-Alder scheme[9] as parametrized by Perdew and Zunger[10]. We use the repeated-slab method to simulate the semiconductor surface. The system is periodic parallel to the surface and we introduced an artificial periodicity perpendicular to the surface, defining a large three-dimensional unit cell. Our slab contained eight layers of GaAs(110) or InP(110) with both sides covered with Sb, and a vacuum region equivalent in thickness to six such layers. Using a (1×1) periodicity parallel to the surface we have constrained ourselves to the examination of the normal modes at the centre of the surface Brillouin zone ($\bar{\Gamma}$ point). For the plane wave basis set we use an energy cutoff equal to 8 Ryd. The **k**-space integration is replaced by a sum over four special points[11] in the irreducible part of the surface Brillouin zone.

In earlier experimental and theoretical works it has been shown that the so called "epitaxially continued layer structure" (ECLS) is the most probable adsorption geometry for Sb on GaAs and InP (110) surfaces. In the present work we have used the fully relaxed geometry in the ECLS[12–15]. Proceeding from this geometry the four atoms of the surface unit cell (two Sb atoms of the overlayer and the cation and anion of the first substrate layer) were treated as coupled three-dimensional harmonic oscillators. These atoms were displaced away from their equilibrium positions and the single-particle wave functions were brought to self-consistency within a global minimization scheme of the total energy functional[16] using the modified scheme of Stumpf and Scheffler[17]. The resulting Hellmann-Feynman forces were fitted to a quadratic equation in the distortion and the linear part was extracted. The cubic dependency of the forces on the distortion was found to be neglectible. A displacement of 0.3 bohr was chosen. Calculations for a distortion of 0.15 bohr resulted in nearly the same force constants (within about 1%), so that the choice of 0.3 bohr seems to be justified, especially if one takes into account that the atomic positions on the surface are less precisely known than within the bulk. To make sure that the forces are coverged with respect to the number of plane waves, some force constants were also calculated using an energy cutoff of 18 Ryd. The maximum deviation in the force con-

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Table I: Comparison of calculated interface frequencies at $\bar{\Gamma}$ with the experimental results of Hünermann *et al* (1991). Frequencies in $\hbar\omega$ / meV.

mode	*first principles*		Raman scattering
	Sb/InP	Sb/GaAs	Sb/InP
Diagonal	44.6	31.4	44.3
(A')	36.4	29.4	40.1
	23.8	26.6	36.1
	20.2	21.7	23.1
	17.3	18.7	19.6
	11.3	11.4	12.0
Nondiagonal	38.9	31.4	36.2
(A'')	18.5	19.3	20.1
	8.3	9.2	missing

stants was found to be 5%. This has led us to conclude that the results obtained with 8 Ryd cutoff would not change qualitatively when the number of plane waves is increased further.

The force constants obtained with 8 Ryd cutoff were used to build up the dynamical matrix. Due to the symmetry of this matrix we end up with more force constants than really needed. This redundancy can be conveniently used to fight any round-off errors in the numerical calculation; by knowing which force constants are equal we average the data obtained from different forces. Once the dynamical matrix $\mathbf{K}$ is specified, solution of the eigenvalue matrix equation

$$\mathbf{M}\ddot{\mathbf{r}} = \mathbf{K}\mathbf{r},$$

where $\mathbf{M}$ contains the masses, yields the surface-atom vibrational normal modes and frequencies.

The point-group symmetry of the surface unit cell is C_S (or m). For the four atoms, group theory yields six optical eigenmodes of symmetry A' with atomic displacements perpendicular to the [$\bar{1}$10] direction and three optical eigenmodes of symmetry A''. Experimentally[2] all six A' modes have been found, but only two A'' modes were detected. In Table I we compare our results with the experimental findings.

Apart from the third A' frequency, where we differ from the experiment by more than 30%, there is at least qualitatively agreement. This mode corresponds to a mixture of a [110] counter movement of one Sb species and the underlying cation atom and an stretching of the Sb chain in [001] direction. The eigenmode A'' which is not found experimentally corresponds to a counter movement of the whole Sb chain against the substrate in [$\bar{1}$10] direction. Although the accuracy of our calculations can always be improved, the results certainly exclude an accidental degeneracy of this mode as assumed by Hünermann *et al* [2]. In their paper they arrange the frequencies not only according to the polarization configurations but also according to the frequency range, so dividing the eigenmodes in Sb derived and substrate derived ones. Our calculations show that the latter division has to be considered carefully.

To make this more clear, we have also solved the eigenvalue problem for the overlayer atoms only, following the approach of Godin *et al* [3]. In Table II the resulting frequencies are given together with the tight-binding

Table II: Comparison of calculated interface frequencies for the overlayer atoms only with tight-binding results of Godin *et al* (1991) and experimental results of Hünermann (1990,1991). Frequencies in $\hbar\omega$ /meV.

mode	*first principles*		tight-binding	Raman scattering	
	Sb/InP	Sb/GaAs	Sb/GaAs	Sb/InP	Sb/GaAs
1A'	12.9	13.4	10.0	12.0	9.2
2A'	16.8	16.4	11.8	19.6	11.1
3A'	22.2	23.0	18.9	23.1	22.5
1A''	18.5	19.3	16.8	20.1	20.75

results and the experimental data of Hünermann[1,2] as given in Richter *et al* [4]. The denotation of modes was chosen in accordance to Fig. 4 in the paper by Godin *et al* [3]. Apart from the A'' mode which is not at all effected by including four instead of two atoms in the surface unit cell, all phonons have changed both in frequency and eigenvector. However if one compares the results obtained by diagonalization of the full dynamical matrix and the one corresponding to the smaller set, it is striking that the agreement between experimental and computational data has not improved by including the substrate. We think that this is rather incidental and for a proper comparison at least 4 surface atoms have to be considered. The agreement between our results and the measured frequencies for Sb/InP is on average 8%. If we do not consider the frequency discussed above which seriously contradicts the experimental findings and the one which could not be found experimentally, the averaged accordance of about 8% is also valid for the results obtained by considering the four atom surface unit cell as given in Table I.

On the other hand, the difference between computational and experimental results for the vibrational modes for Sb/GaAs as given in Table II is appreciable. Hünermann[1] reports that the interface peaks for 1ML of Sb on GaAs(110) were generally less pronounced than on InP(110). The most pronounced peak corresponds to the $1A''$ mode which we also find in reasonable agreement with the experiment (within 7%). We find all other modes in the Sb range quite close to the ones we obtained for the InP case. To our mind this is reasonable since the adsorption energies of Sb on GaAs and InP are nearly the same[14,15] and we expect therefore a similar strength of bonding between the overlayer and the substrate and within the Sb-chain. In the substrate range the mass differences between the substrate species causes different frequencies.

A so called "epitaxial on top structure" (EOTS) has also been proposed by LaFemina *et al* [18] for an ordered 1ML coverage of Sb on III-V(110). This structure has been found to be less favourable in terms of energy and leads to somewhat longer bond lengths between the overlayer and the substrate[14]. If we assume this geometry for Sb/GaAs(110) and calculate the eigenmodes for the overlayer atoms only, we end up with frequencies (in meV) for the A' modes of 13.1, 15.0 and 21.6 whereas we find the A'' mode at 17.9 meV. It is interesting to note that firstly these values provide worse agreement with experiment and secondly all these frequencies are lower compared to the ones we calculated for the ECLS, due to the weaker bonding between the overlayer and the substrate.

In summary, we have made first-principles calculations of interface phonons of an epitaxial Sb monolayer on GaAs(110) and InP(110). In the case of Sb/InP(110) our results compare well with experimental data. For Sb/GaAs(110) the agreement between experimental values and both earlier tight-binding results and our calculations is not satisfactory. This might be due to reported experimental difficulties in finding pronounced peaks for this overlayer system.

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