Structural, electronic, and dynamical properties of Si(110) capped with a monolayer of GaAs

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Using a first-principles pseudopotential technique, we have presented structural and electronic properties of the Si(110) surface capped with a monolayer of GaAs. These results are further used to investigate the phonon-dispersion curves and the phonon density of states of the system. Both an adiabatic bond-charge model and a linear-response scheme to the *ab initio* pseudopotential method have been employed for the study of the phonon properties, and the results obtained from the two methods are compared systematically. The surface acoustic-phonon modes of this system have energies similar to those on the clean GaAs(110) surface, while the highest surface optical-phonon mode of this system lies at a higher energy than the corresponding mode for the clean GaAs(110) surface. These and other similarities and dissimilarities between the GaAs:Si(110) and GaAs(110) surfaces are discussed and explained.

I. INTRODUCTION

In recent years a great deal of effort has been devoted to the study of the growth of GaAs on Si substrates. The reason for choosing this study is that GaAs and Si are very important in semiconductor technology, and understanding their structural, electronic, and vibrational properties will help to understand their many varied applications in devices. For example, Si can be used in electronic devices such as diodes and transistors while GaAs is a very good choice for optical devices (lasers, light detectors) due its direct band gap. Consequently, the structural and electronic properties of GaAs on Si(111) (Refs. 1–3) and Si(001) (Refs. 4–7) surfaces have recently attracted a great deal of attention.

In contrast, however, relatively less attention has been paid to the growth of GaAs on the Si(110) surface because of difficulties in preparing a clean Si(110) surface. However, the last few years have witnessed substantial progress in experimental studies of the clean Si(110) surface[8,9] and the deposition of metal monolayers on this surface.[10–13] To date, properties of the adsorption of a single monolayer of GaAs on Si(110) have been only studied by Rodriguez and Takeuchi.[14] From their first-principles calculations,[14] they have shown that the most stable configuration corresponds to the GaAs monolayer adsorbed on top of the Si(110) substrate. This model has a relaxation pattern similar to the III-V(110) surfaces: As atoms move away from the surface, Ga atoms move within the surface. As result of this similarity, the *ab initio* calculations[14] revealed that the structural and electronic properties of GaAs:Si(110) and clean GaAs(110) surfaces are similar. In fact, the most striking difference between these surfaces is the mass difference between Si and Ga (or As) atoms. Thus, surface lattice dynamics can be used as a potential tool for characterizing the GaAs:Si(110) system. In addition, knowledge of dynamical properties will be useful in understanding surface reconstruction, phase transition, and the relaxation process of electronically or vibrationally excited states.

In this paper, results of *ab initio* calculations for structural, electronic, and dynamical properties of GaAs:Si(110) are presented and discussed. We have used our calculated structural and electronic results as input to further calculate the vibrational properties of this system. This we have achieved at two different levels. On one hand we have employed the linear-response approach, within the pseudopotential theory and the local-density scheme, using the computer code discussed in Ref. 24. On the other hand we have used the surface structural and electronic information to set up and solve the dynamical matrix within the adiabatic bond-charge model. This choice was made in view of the fact that this model takes significantly less computational effort and time to calculate the full dispersion relation and the density of phonon states, and has previously been successfully applied to the Si(001) (2×1) (Ref. 15) and III-V(110) surfaces.[16,17] The results obtained from the two theoretical methods also allow us to compare the phonon-dispersion curves from *ab initio* and bond-charge model (BCM) calculations in detail. In addition we have compared the surface phonon modes on the GaAs:Si(110) surface with those on the GaAs(110) surface obtained previously from both the *ab initio* (Refs. 18,19) and BCM (Ref. 16) calculations.

We have found that the zone-center phonon modes identified for the clean GaAs(110) surface can also be observed for the GaAs:Si(110) surface. We have also observed that surface phonon modes with energies higher than 40 meV are mainly localized on the second- and third-layer atoms due to the large mass difference between Si and Ga (or As) atoms. Displacement patterns for a representative selection of phonon modes with both theoretical models have been presented at the zone center and zone edges.

II. THEORY

A. *Ab initio* pseudopotential density-functional theory

Our calculations were performed in the framework of the density-functional theory, within the local-density approximation using the Ceperley-Alder correlation[20] as parametrized by Perdew and Zunger.[21] Ion-electron interactions are
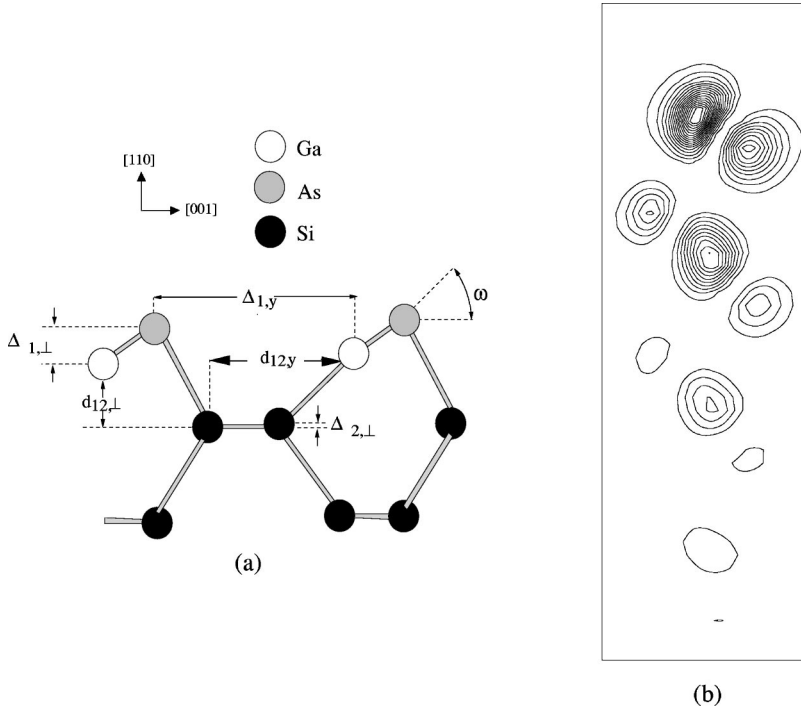
FIG. 1. (a) Schematic relaxed side view of GaAs:Si(110). (b) The electronic charge density for the occupied dangling-bond state.

treated by using norm-conserving pseudopotentials.[22] The wave functions were expanded in a plane-wave basis set with a kinetic-energy cutoff of 12 Ry. Relaxation of atomic and electronic degrees of freedom was achieved by solving the Kohn-Sham equations. We considered an artificially constructed periodic geometry along the surface normal direction. The length of the unit cell was equivalent to 19 atomic layers. The slab contained 13 layers of Si atoms, and two layers of GaAs which were placed on the top and bottom of the silicon slab. All atoms were allowed to relax into their minimum-energy configuration, except for the atoms in the middle of the slab which were kept frozen. Four special **k** points were used for sampling the irreducible segment of the Brillouin zone.

The phonon-dispersion curves have been obtained by applying the density-functional perturbation scheme within the pseudopotential theory,[23] using the computer code discussed in Ref. 24. The dynamical matrices were calculated for the relaxed atoms in the supercell by determining the static linear response of the electrons for periodic displacements of the atoms from their equilibrium positions. One-dimensional Fourier interpolation has been used to obtain phonon dispersions along the main surface symmetry directions. In particular, we calculated the dynamical matrix at five q points along each of the $\bar{\Gamma}$-$\bar{X}$ and $\bar{\Gamma}$-$\bar{X}'$ directions.

B. The adiabatic bond-charge model

As the second theoretical model for surface phonon calculations, we employed Weber's adiabatic BCM (Ref. 25) as described in our previous works.[15–17] The interactions included in the BCM are the Coulomb interaction between all particles including ions and bond charges (BCs) (ion-ion, ion-BC, and BC-BC), a central short-range interaction between the nearest-neighbor particles, and a bond-bending interaction involving the BC-ion-BC angle. In order to be able to study lattice dynamics of GaAs:Si(110) surfaces, we applied this model within a repeated slab scheme. Our supercell was of same size as used in the *ab initio* calculations, described in the previous subsection. Our relaxed unit cell contained 30 ions (26 Si, 2 Ga, and 2 As) and 60 BCs. The BCs between Ga and Si atoms were displaced towards Si atoms, dividing a bond in the ratio 3:4 while the BCs between Si and As atoms were displaced towards As atoms, dividing a bond in the ratio 4:5. The positions of the dangling BCs were determined from the maximum in the valence-electron density plot obtained from our density-functional calculations (see Fig. 1). The second derivatives of the central ion-ion and ion-BC potentials (ϕ'') involving surface atoms were scaled as $\phi''_{surface} = r^2_{bulk}/r^2_{surface}\phi''_{bulk}$, where r_{bulk} and $r_{surface}$ denote the magnitude of the relative distances between particles.

III. RESULTS

A. Structural and electronic properties

The calculated structural parameters of the GaAs:Si(110) surface, defined in Fig. 1, are listed in Table I. The results

TABLE I. Structural parameters, defined in Fig. 1, for a monolayer of GaAs on Si(110).

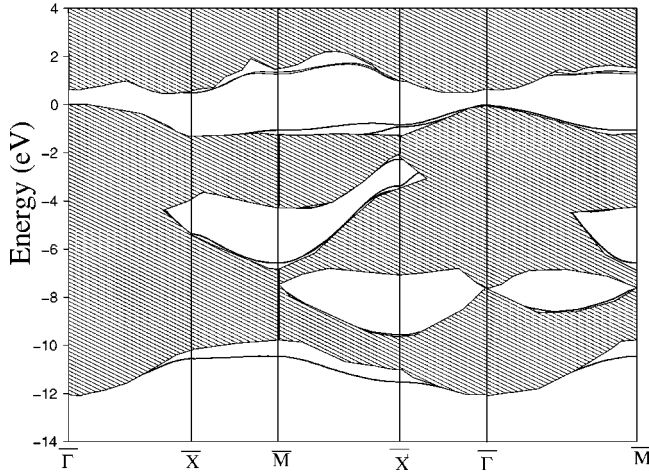|	a(Å)	$\Delta_{1\perp}$ (Å)	Δ_{1y} (Å)	$\Delta_{2\perp}$ (Å)	$d_{12\perp}$ (Å)	d_{12y} (Å)	ω (deg)
Present	5.41	0.66	4.15	-0.04	1.51	3.10	27.6
Reference 14	5.43	0.62	4.17	-0.02	1.51	3.08	26.0

FIG. 2. The electronic structure of the GaAs:Si(110) surface. The projected bulk spectrum is shown as hatched regions. The surface localized states, occupied as well as unoccupied, are shown by thick solid curves.
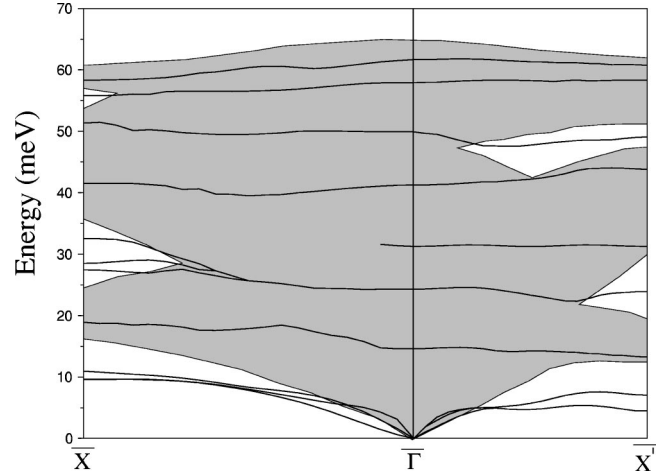

FIG. 3. The dispersion of phonon modes on GaAs:Si(110). The results for surface phonon modes are shown by thick lines while the projected bulk phonon energies are shown as hatched regions.

follow the trend observed for the clean GaAs(110) surface. The surface layer As atoms move away from the bulk in favor of an $s^2 p^3$ bonding with three neighboring atoms (one Si and two Ga atoms), resulting in a pyramidal geometry. The surface Ga atoms move into the bulk in favor of an sp^2 bonding with three neighboring atoms (one Si and two As atoms). In general, our structural parameters are in agreement with the recent *ab initio* calculations by Rodriguez and Takeuchi.[14] In particular, our calculated tilt angle of the top surface layer at 27.6 ° can be compared with that at 26.0 ° in the work of Rodriguez and Takeuchi.

Figure 2 presents the electronic structure of the GaAs:Si(110) surface along the symmetry directions. The projection of the band structure of the homopolar semiconductor Si on the (110) surface shows a continuous energy distribution of its valence bands, except for a few pockets or "stomach gaps" in which no bulk states are found. There are no surface states for GaAs:Si(110) falling well inside these stomach gaps. The lowest occupied surface state shows a truly localized behavior along $\bar{X}$-$\bar{M}$-$\bar{X'}$ on the surface Bril-

louin zone. The highest occupied state lies slightly above the bulk valence-band continuum along $\bar{M}$-$\bar{X'}$ and is made of the sp^3-like orbital of the dangling bond at the surface arsenic atoms.

B. Dynamical properties

1. Ab initio results

The phonon spectrum for the GaAs:Si(110) surface is plotted in Fig. 3. The results for surface phonon modes are shown by thick lines while the projected bulk phonon energies are shown as hatched regions. A few general observations can be made. Because of the mass difference between Si and Ga (or As) atoms, the surface acoustic modes on the GaAs:Si(110) surface turn into truly localized states. Interestingly, the energy locations of these waves are very similar to those for the clean GaAs(110) surface.[16] The highest-lying phonon state for the GaAs:Si(110) surface lies into the bulk optical range of bulk Si. Near the surface Brillouin-zone boundaries we have observed localized surface modes.

TABLE II. The zone-center phonon frequencies of the GaAs:Si(110) surface from the *ab initio* and the BCM calculations. Results are also compared with the zone-center phonon modes of the clean GaAs(110) surface. SZCM and SSZCM indicate surface layer and subsurface layer zigzag chain modes while RM and BCM indicate rotational and bond-stretching phonon modes.

Surface	A'' modes			A' modes			
GaAs:Si(110)$^{ab\ initio}$	31.3	57.9	61.6	14.6	24.3	41.3	50.0	57.9
GaAs:Si(110)^{BCM}	30.9	56.5	61.4	13.7	25.9	40.9	51.7	56.6
GaAs(110) [a]	31.1		31.7		23.7			
GaAs(110) [b]				11.1	23.2			
GaAs(110) [c]	28.7		32.2	10.99	22.8			
	SZCM		SSZCM	RM	BCM			

[a]Reference 18.
[b]Reference 19.
[c]Reference 16.

TABLE III. Comparison of the *ab initio* and BCM results for the GaAs:Si(110) surface at the $\overline{X'}$ point.

Source	A'' modes				A' modes			
GaAs:Si(110)$^{ab\ initio}$	4.5	31.3	7.0	24.0		43.8	49.0	57.9
GaAs:Si(110)^{BCM}	5.3	30.6	6.0	21.2	27.5	43.9	48.4	56.6

It is convenient to separate the zone-center surface modes according to their polarization characteristics: A'' if the vibrations are along the zigzag atomic chain (i.e., along $[\bar{1}10]$), and A' if the vibrations take place in the sagittal plane defined by the [001] and [110] directions. Table II lists a selected number of zone center of A' and A'' modes. The lowest-lying mode (an A' mode) is a rotational phonon mode with opposing motion of surface layer atoms. The energy of this phonon mode is nearly 3-meV higher than that on the clean GaAs(110) surface,[16] which can be related to the smaller mass of the substrate Si atoms which affect this mode. The mode at 24.3 meV has a large bond-stretching character. The A' phonon mode at 41.3 meV includes large atomic vibrations from the second-layer Si atoms.

The surface phonon modes with a group symmetry representation A'' are found at energies of 31.3 meV and 61.6 meV. The lower-lying mode is a surface zigzag chain mode (SZCM), and can be identified with a similar mode at 31.1 meV for the clean GaAs(110) surface.[18] The identification of the SZCM on GaAs:Si(110) with that on the clean GaAs(110) becomes possible because of its total localization on the first-layer atoms. However, it should be pointed out that this mode has different polarization for the two systems. In our previous works, we have identified the highest surface optical frequency of III-V(110) surfaces[16,17] with A' character, but for this surface this phonon mode shows the A'' character with opposing motion of second-layer atoms in the zigzag chain direction.

Table III presents a selected number of A' and A'' modes at the zone-edge point $\overline{X'}$. At this point the Rayleigh wave (RW) is localized and corresponds to the motion of the top two-layer atoms in the zigzag chain direction. It is important to note that this phonon has the A'' group symmetry representation, while the RW phonon mode on III-V(110) surfaces[16,17] has the A' character. For this surface, the second lowest acoustic phonon mode is obtained at 7.0 meV. The phonon modes at 24.0 and 49.0 meV are localized gap phonon modes, while the phonon mode at 31.3 meV is a surface layer zigzag chain mode at the zone edge. Figure 4 displays the atomic displacement patterns of the RW and the localized gap phonon modes at the $\overline{X}$ point. The energy of the RW is only 1-meV higher than that on the clean GaAs(110) surface. This phonon mode includes larger atomic vibrations from first As atom and its neighbor Si atom. The phonon modes at 27.5, 28.5, and 32.6 are stomach gap phonon modes at $\overline{X}$. The phonon mode at 55.8 meV lies in the upper gap region. For this phonon mode, the surface layer atoms (viz., Ga and As) do not vibrate due to their relatively heavier masses.
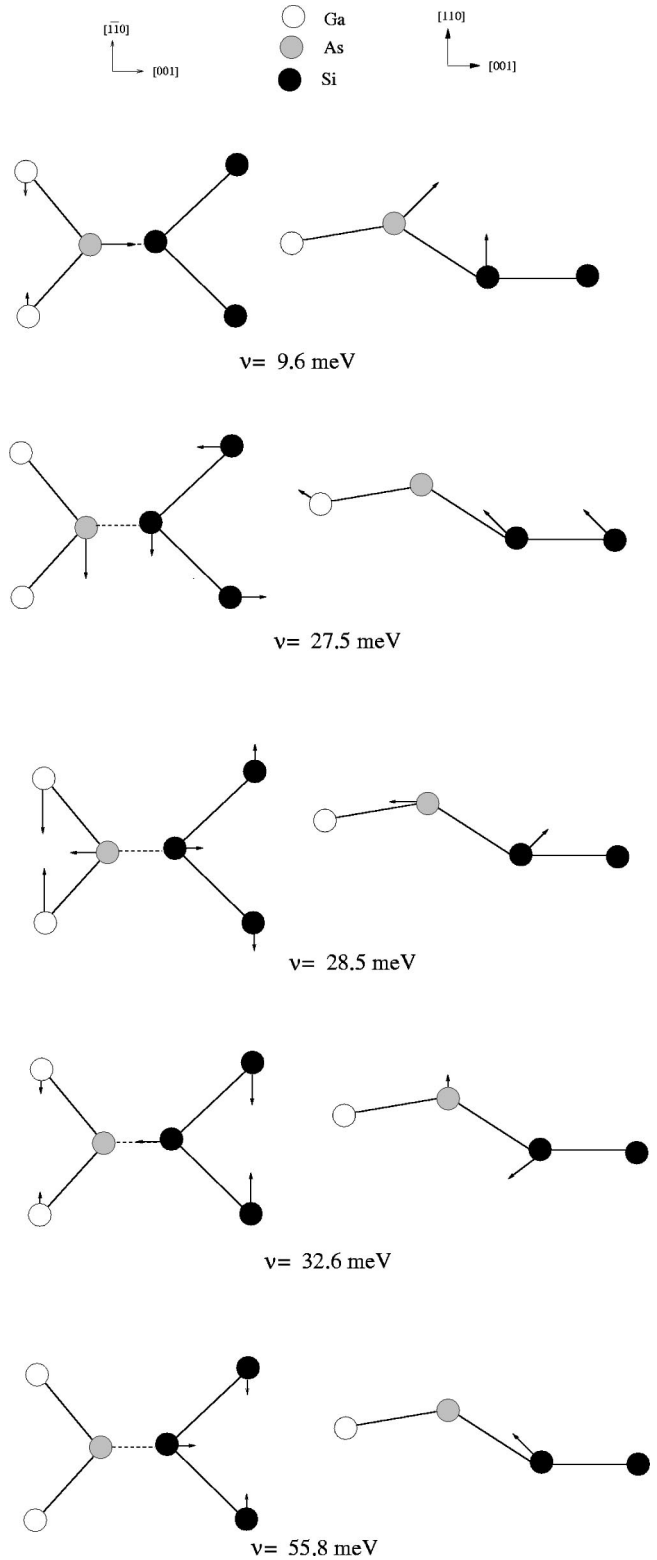
FIG. 4. Atomic displacement patterns of Rayleigh wave (RW) and localized gap phonon modes at the $\overline{X}$ point.

2. BCM results

As the bond-charge model (BCM) provides a comparatively much easier method for setting up the dynamical matrix, we have plotted in Fig. 5 the phonon dispersion along
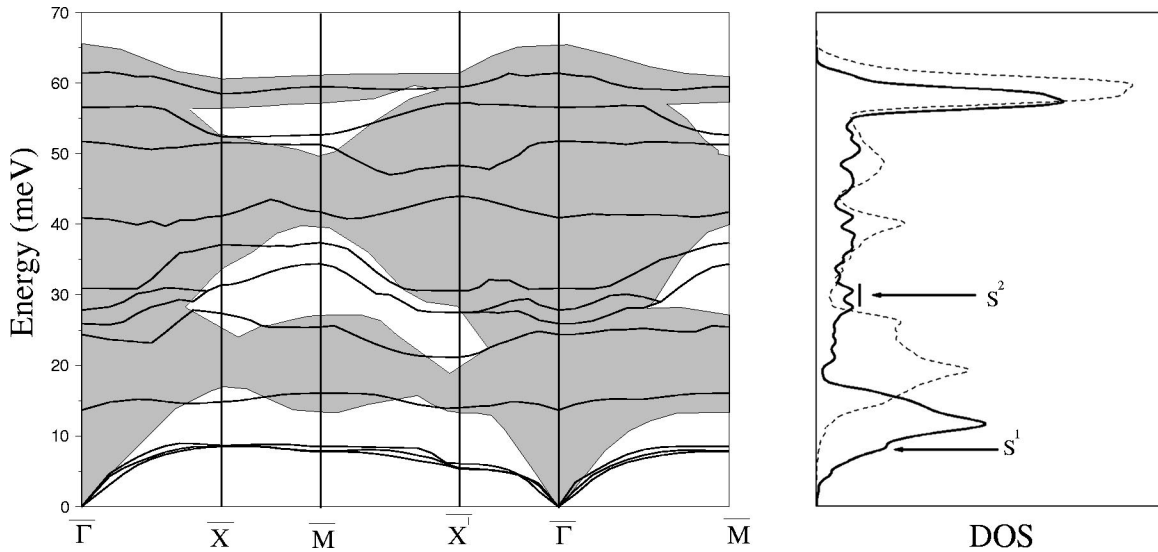
FIG. 5. Dispersion of phonon modes and the density of states on the GaAs:Si(110) surface obtained from the adiabatic bond-charge model. The calculated surface results are shown by solid lines, and the bulk results are shown by hatched regions and a dashed line (in the density of states).

five symmetry directions and the density of states. The BCM calculations clearly show that surface acoustic frequencies are localized phonon modes for large parts of the surface Brillouin zone. The peak S^1 in the phonon density of states is due to surface acoustic-phonon modes, and the peak S^2 is characterized by the stomach gap phonon modes.

At the zone center we identify a rotational phonon mode at 13.7 meV and a bond-stretching phonon mode at 25.9 meV. The atomic displacement pattern for these modes is similar to those obtained from the *ab initio* calculation. The surface layer and subsurface layer zigzag chain modes are identified at 30.9 and 61.4 meV, respectively. At the $\overline{X'}$ point, our BCM calculations also predict two acoustical-phonon frequencies at 5.3 and 6.0 meV (see Table III). The second one has A' character while the first one has A'' character. The localized gap phonon modes at this **q** point are found at 27.5 and 48.4 meV. We have also identified a zigzag chain phonon mode at 30.7 meV. At the $\overline{X}$ point we have identified the RW mode at 8.5 meV, and two localized gap modes at 27.4 and 31.3 meV. The atomic displacement patterns for these are shown in Fig. 6. An inspection of Fig. 6 along with Fig. 4 indicates that there is some difference in the atomic displacement patterns corresponding to the Rayleigh phonon mode (RW) obtained from the BCM and *ab inito* methods. This difference can be due to very small mass difference between Ga and As atoms: our BCM calculation predicts large atomic vibrations from Ga atoms while our *ab initio* calculation predicts large atomic vibrations from As atoms. It should be pointed out that a similar difference has found in the bulk atomic vibrations of GaAs: in the BCM model the longitudinal-acoustic phonon mode at the X point of the bulk Brillouin zone is due to the vibration of a Ga atom, while in the *ab initio* model this phonon mode is characterized by the motion of an As atom.

3. Further discussion of results

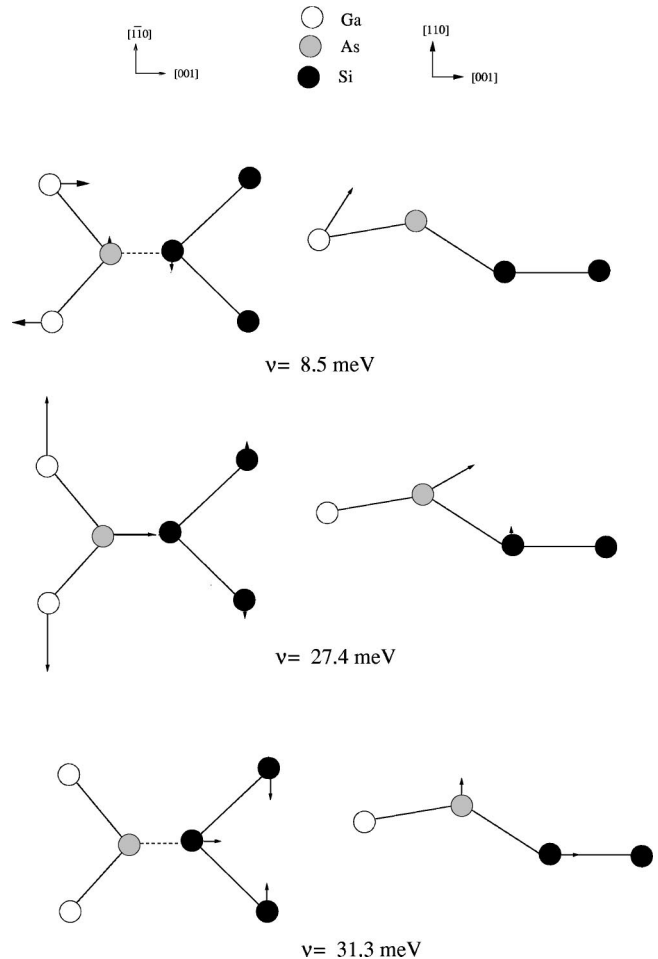It is useful to gain overall confidence in surface phonon results obtained from a simple and semiempirical method

FIG. 6. Atomic displacement patterns of the Rayleigh wave (RW) and localized gap phonon modes with the BCM model at the $\overline{X}$ point.
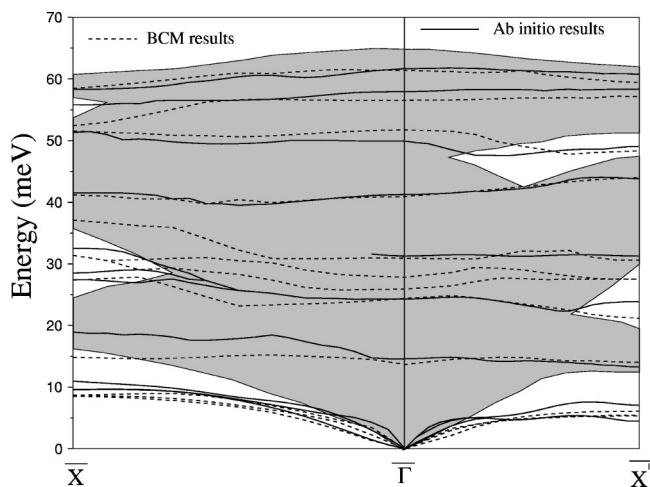
FIG. 7. Comparision of the phonon modes obtained from the *ab initio* and BCM calculations for the GaAs:Si(110) surface.

such as the BCM. With this in mind we have plotted our *ab initio* and BCM results together in Fig. 7. In general, the results from both calculations are in very good agreement with each other. In Table II we have presented a comparison of the energies of the zone-center modes obtained from the two methods. For comparison, in this table we have also included the zone-center phonon modes on the clean GaAs(110) surface.

As a general remark we note that the rotational, bond-stretching, surface layer zigzag chain and subsurface layer zigzag chain phonon modes predicted for the clean GaAs(110) surface have also been identified for the GaAs:Si(110) surface. The rotational, bond-stretching, surface layer zigzag chain phonon modes for both the GaAs(110) and GaAs:Si(110) surfaces have comparable energies. However, there is a large energy difference between the subsurface-layer zig-zag chain mode on GaAs(110) and GaAs:Si(110). This is not surprising, since this phonon mode is due to the motion of second-layer atoms, which have different reduced masses for the two systems.

Table III presents a comparison of the *ab initio* and BCM results at the zone-boundary point $\overline{X}'$. Clearly, on the whole the results from both calculations agree very well with each other. The only significant difference occurs for the modes in the lower stomach gap region. The maximum difference occurs for the second lowest A' mode, with the BCM result being approximately 3-meV higher. The BCM calculations predict two phonon modes in this gap region while the *ab initio* calculations predict only one phonon mode. This difference can also be seen at the $\overline{X}$ point, where the *ab initio* and BCM calculations predict three and two phonon modes, respectively.

IV. SUMMARY

In this paper, the structural and dynamical properties of the GaAs:Si(110) surface have been investigated and discussed by employing the *ab initio* pseudopotential theory. In addition, phonon-dispersion curves and density of states for this surface have also been studied by employing the adiabatic bond-charge model. In general, the calculated phonon-dispersion curves from both methods agree very well, except for some differences in the stomach gap regions. Both theoretical models have predicted that the zone-center phonon modes between energies of 10 and 36 meV are characterized by displacement patterns similar to those on the clean GaAs(110) surface. Similarly, we find that the RW phonon mode on this surface has a similar energy location to that on the clean GaAs(110) surface. However, we have observed that the vibrational pattern of the RW phonon mode at the $\overline{X}'$ point is different from that on the clean GaAs(110) surface. Notably, the high-frequency (i.e., above approximately 40 meV) phonon modes throughout the surface Brillouin zone are mainly localized in the substrate, with very little motion of the adsorbate layer atoms. This is entirely to be expected, because of the significantly smaller mass of Si compared to Ga and As. The present work leads us to conclude that adsorption of heavier atom(s) on surfaces can be expected to be well characterized by low-lying surface modes, and in particular low-lying localized Rayleigh phonon modes.

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