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Phonon spectrum and density of states on GaAs(001)-$\beta_2(2\times4)$

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We have studied the lattice dynamics of the GaAs(001)-$\beta_2(2\times4)$ surface by employing two theoretical methods: an *ab initio* pseudopotential method and a phenomenological adiabatic bond-charge method. Both methods predict a number of surface localized phonon modes. Most of these modes are found to lie at similar energy locations from both methods. However, the two methods produce eigenvectors of some of the modes which are at variance with each other. Possible reasons for such differences are outlined. Particular emphasis has been laid on the discussion of the highest surface phonon mode, which lies above the bulk continuum. A brief discussion of the role of this mode in examining surface reactions has also been provided.

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I. INTRODUCTION

The GaAs(001) surface has been among the most widely studied of semiconductor surfaces because of its importance for the growth of multilayer device structures. Over the past two decades, most experimental[1–8] and theoretical[9–16] works have been devoted to the determination of surface atomic geometry and surface electronic states. The (2×4) reconstructed surface, occurring during normal As-rich growth conditions, is one of the best understood. Three different phases of the (2×4) surface have been identified by Farrell and Palmstrom.[4] Depending on the temperature of the interruption of the As flux, these phases are denoted as α, β, and γ, corresponding to the surface monolayer (ML) As coverages of 0.5, 0.75, and 1 ML, respectively. In particular, the stability of the As-terminated GaAs(001)-$\beta_2(2\times4)$, with a 0.75 ML coverage of As, has been extensively verified experimentally.[2,4–8]

The atomic structure of the GaAs(001)-$\beta_2(2\times4)$ surface has been determined by using the scanning tunneling microscopy[2,5,6] and x-ray diffraction technique.[8] The accepted geometry of the GaAs(001)-$\beta_2(2\times4)$ surface is that the top surface layer contains two As dimers and two missing As dimers, the second layer is characterized by missing Ga atoms beneath the two missing As dimers in the top layer, and there is one As dimer in the exposed third layer.[9,11,12] Detailed *ab initio* pseudopotential calculations have been performed[13–16] to investigate the atomic geometry, electronic structure, and chemical bonding on this surface.

In contrast to the wealth of work presented in recent years on the structural and electronic properties of this surface, only a limited amount of information is available on the vibrational properties of this surface. Generally, three experimental techniques have been employed to investigate surface phonon modes: inelastic particle scattering methods, such as helium atom scattering; electron spectroscopic techniques, such high resolution electron energy loss spectroscopy (HREELS); and optical techniques, such as Raman scattering, infrared adsorption, and second-harmonic generation (SHG). Phonon modes on H-GaAs(001)-$c(8\times2)$ have been investigated by HREELS.[17] A time-resolved SHG technique[18] has been employed to detect phonon modes on a Ga-rich GaAs(001) surface with reconstructions (1×6), (4×6), and (4×1). However, there seem to be no reports of phonon detection on As-rich GaAs(001) surfaces. Only recently, we have calculated zone-center phonon modes for the As-rich GaAs(001)-$\beta_2(2\times4)$ surface using a linear response approach based on the density-functional and pseudopotential theories.[19] A full-scale surface phonon study is expected to be very valuable for obtaining additional signatures of surface reconstruction, for electron-phonon interaction, and for further studies related to phase transition and relaxation processes involving electronically or vibrationally excited states.

In this work, results of *ab initio* calculations for structural properties of the GaAs(001)-$\beta_2(2\times4)$ surface have been presented and discussed. Our structural results are in good agreement with previous experimental[8] and theoretical[15,16] calculations. Using our structural results, we have calculated surface phonon modes on this surface by employing two different theoretical methods: using a linear response approach, based on an *ab initio* pseudopotential method and the local density-functional perturbation scheme,[20] and an empirical adiabatic bond-charge model.[21,22] We have determined energy locations and polarization characteristics of several interesting phonon modes, including rocking, dimer stretch, and highest surface optical phonon modes from both theoretical models. Surface phonon dispersion curves obtained from both models are compared against each other in detail. In general, we have found that the results from both models are in good agreement with each other. However, some differences have been noted for atomic displacement patterns of higher energy surface phonon modes. We believe that these differences are due to differences in the conceptual natures of the theoretical methods employed.

II. THEORETICAL METHODS

A. Ab initio pseudopotential density-functional theory

Our theoretical treatment of surface structural determination is based on the density-functional theory in the local density approximation using the Ceperley-Alder correlation,[23] as parametrized by Perdew and Zunger.[24] The electron-ion interaction was treated by using norm-conserving pseudopotentials.[25] Single particle wave functions were expanded in a plane-wave basis, with a kinetic energy cutoff of 15 Ry. The theoretical lattice constant of 5.60 Å was used for all calculations. In order to apply the plane-wave formalism to the GaAs(001)-$\beta_2(2\times4)$ surface, we considered an artificially constructed periodic geometry along the surface normal direction. The unit cell contained eight atomic layers and a vacuum region equivalent to twice the bulk lattice constant. Self-consistency in solutions to the Kohn-Sham equations[26] was achieved by considering four **k** points within the irreducible part of the Brillouin zone. In order to obtain a relaxed atomic geometry, the Ga-terminated back surface of the slab was saturated with fractionally ($Z=1.25$) charged H atoms. Each atom was allowed to move with the exception of the atoms on the two bottom layers of the slab. The equilibrium positions were determined within an atomic force tolerance of approximately 0.1 mRy/a.u.

In order to study the surface phonon spectrum of the surface, we used the density-functional perturbation theory.[20] Within this scheme, second-order derivatives of the total energy were calculated to obtain the dynamical matrix. A static linear response of the valence electrons was considered in terms of the variation of the external potential corresponding to periodic displacements of the atoms in the supercell. The screening of the electronic system in response to the displacement of the atoms was taken into account in a self-consistent manner. For bulk phonons, we calculated dynamical matrices for a $4\times4\times4$ mesh of phonon wave vectors **q** inside the irreducible part of the bulk Brillouin zone. Three-dimensional Fourier interpolation was carried out to calculate bulk phonons for any chosen **q** point. For surface phonon calculations, we calculated dynamical matrices corresponding to a $4\times4\times1$ **q** point mesh within the irreducible segment of the surface Brillouin zone and carried out a two-dimensional Fourier interpolation to obtain surface phonons for any chosen **q** point.

B. Adiabatic bond-charge model

As the second theoretical model for surface phonon calculations, we have employed Weber's adiabatic bond-charge model (BCM),[21,22] as described in our previous papers.[27,28] The main idea in this model is that the valence electron charge density distribution is represented by massless bond charges (BCs), endowed with translational degrees of freedom. The BCs in homopolar semiconductors are positioned in the middle of interatomic bonds, while in III-V semiconductors they are displayed toward anions, dividing a bond in the ratio 3:5. If r_0 indicates a bond length and $r_1=\frac{(1+p)r_0}{2}$ and $r_2=\frac{(1-p)r_0}{2}$ indicate cation-BC and anion-BC distances, respectively; then, the ionicity parameter p is considered to take the values 0.0 and 0.25 for IV and III-V semiconductors, respectively.

In order to calculate lattice dynamical properties of the GaAs(001)-$\beta_2(2\times4)$ surface, we have used a repeated slab scheme. Our supercell was of the same size as used in the *ab initio* calculations and thus contained 58 ions (from 30 Ga and 28 As atoms) and 84 bulklike BCs placed toward the anions, dividing a bond in the ratio 3:5. Dimer bond charges were placed in the middle of As-As bonds. Moreover, 16 H atoms in the Ga-terminated surface of the slab were replaced with 16 dangling BCs. Thus, we have a total of 103 BCs in the supercell. The interactions included in the BCM are the Coulomb interaction between all particles (ion-ion,ion-BC, and BC-BC), a central short-range interaction between nearest neighbor particles, and a bond-bending interaction involving BC-ion-BC angles. The bond-bending potential is expressed as

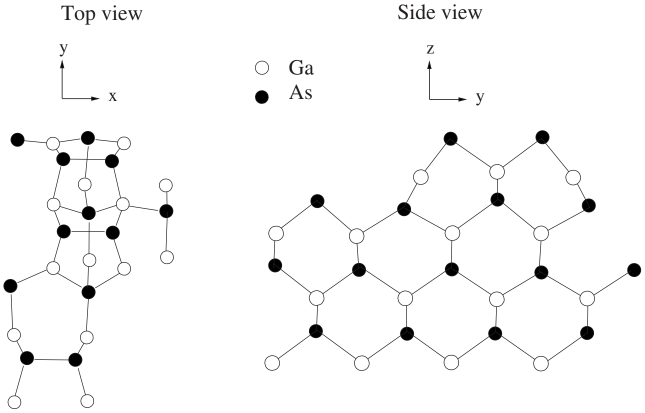

FIG. 1. Top and side views of the relaxed atomic geometry of the GaAs(001)-$\beta_2(2\times4)$ surface.

$$V_{bb}^{\Delta}=\frac{1}{2}B_{\Delta}(r_{\Delta i}r_{\Delta j}+a_{\Delta}^2)^2/4a_{\Delta}^2, \qquad (1)$$

where $r_{\Delta k}$ is the distance vector between the ion type Δ and its neighboring bond-charge k, a_{Δ}^2 is the equilibrium value of $|r_{\Delta i}r_{\Delta j}|$, and B_{Δ} is the bond-bending force constant. Although the bond-bending force constant parameters B_1 and B_2 are taken at their bulk values, the elements of the short-range bond-bending ion-BC matrices between the top-layer atoms and their neighboring BCs generally become very different from their bulk values because the dot product $r_{\Delta i}r_{\Delta j}$ for neighboring BCs changes considerably on the relaxed surface. Moreover, the lattice vibrations of atoms near the surface are expected to have frequencies different from those of bulk vibrations since, as on the vacuum side of the surface, the restoring forces are missing. To account for the effect of surface relaxation, the second derivatives of the central ion-ion and ion-BC potentials (ϕ'') involving surface atoms were scaled as $\phi''_{surface}=(r_{bulk}^2/r_{surface}^2)\phi''_{bulk}$, where r_{bulk} and $r_{surface}$ denote the magnitude of the relative distances between particles.

III. RESULTS

A. Atomic geometry and electronic states

Our calculated relaxed geometry of the GaAs(001)-$\beta_2(2\times4)$ surface, shown in Fig. 1, is in full agreement with previously reported theoretical results (see, e.g., Refs. 15 and 16) and experimental results (see, e.g., Ref. 8). The bond

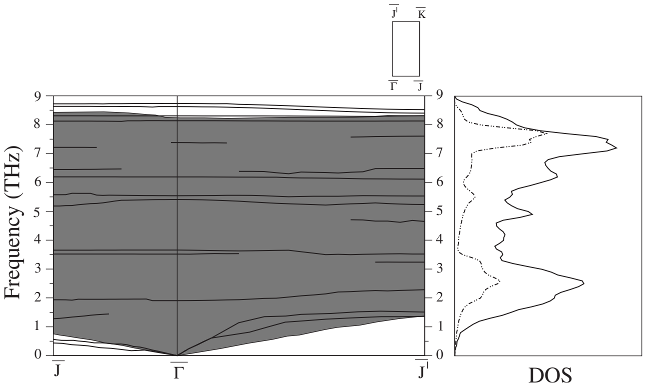

FIG. 2. Surface phonons and density of states on the GaAs(001)-$\beta_2(2\times4)$ surface. The calculated results are shown by thick curves, while the bulk results are shown by the hatched region for the dispersion curve and dashed lines for the density of states.

lengths of the As-As dimers on the top and third atomic layers are approximately 2.48 Å, and the minimum vertical separation between the top and second atomic layers (i.e., between As atoms in the top-layer and fourfold coordinated Ga atoms in the second layer) is 1.49 Å. The second layer is characterized by a vertical buckling of about 0.26 Å between the threefold and fourfold coordinated Ga atoms, with threefold Ga atoms lying lower. The threefold and fourfold Ga atoms are involved in a bimodal distribution of bond lengths. The bond length between threefold coordinated Ga and its neighboring As atoms (in the top and third layers) is 2.37 Å. This bond length is approximately 5% smaller than the bond length of 2.50 Å between a fourfold coordinated Ga and its As neighbors in the top layer.

The top two, and closely lying, occupied surface states of the π^* character are found just below the top of the bulk valence band and originate from the third- and top-layer As-As dimers. The lowest unoccupied surface state lies just below the bulk conduction band minimum and originates from the empty dangling bond on the Ga atoms in the second layer. These features are similar to previously reported results (e.g., Ref. 16).

B. Dynamical properties

1. Ab initio phonon results

The phonon spectrum of the GaAs(001)-$\beta_2(2\times4)$ surface, together with the projection of the GaAs bulk results, is displayed in Fig. 2. Starting from the $\bar{\Gamma}$ point in both symmetry directions, we observe two branches of surface phonons above the projected bulk spectrum. These branches are flat along the $\bar{\Gamma}$-$\bar{J}$ direction (i.e., along the ×4 reconstruction), while they show a little dispersion along the $\bar{\Gamma}$-$\bar{J'}$ direction (i.e., along the ×2 reconstruction). A further prominent feature is the extremely flat branch, along both symmetry directions, with a frequency of 6.2 THz. The flatness of this branch leads to a peak in the phonon density of states (DOS). Just below this peak, there is a clear surface phonon peak in the density of state curve due to a flat branch close to 5 THz in the surface phonon spectrum. In addition to these strong surface peaks, we have also observed two small DOS peaks in the frequency range 3–5 THz. These peaks arise due to the flatness of surface states in the phonon spectrum at the corresponding frequency range and produce small but interesting features compared with a smooth variation of the bulk DOS in this interval. The most interesting feature is the surface optical phonon mode situated at around 3.6 THz. This flat branch results from a rocking motion of the atoms in the surface region and can be interpreted as a dynamical version of the surface relaxation. Two surface acoustic phonon branches appear in the surface phonon spectrum along both symmetry directions. We have observed that these branches become more distinct from the bulk phonon modes along the $\bar{\Gamma}$-$\bar{J}$ direction.

At the $\bar{\Gamma}$ point, we have identified 11 surface phonon modes with frequencies 1.90, 3.52, 3.63, 5.54, 5.87, 6.33, 7.13, 8.14, 8.30, 8.60, and 8.74 THz. Only one of these includes large atomic vibrations from the third-layer dimer atoms. The frequency of this phonon mode is 3.63 THz. This phonon mode can be classified as a dimer rocking mode due to the opposing motion of third-layer As dimer atoms. Displacement patterns of other surface phonon modes are shown in Fig. 3. The low frequencies at 1.90 and 3.52 THz describe the opposing motion of the first-layer dimer atoms with components in both dimer bond and surface normal directions. These phonon modes also include atomic vibrations from both threefold and fourfold coordinated Ga atoms. We have observed a bond stretching character between a threefold Ga atom and its three neighboring As atoms for the phonon mode at 5.54 THz. The parallel motion of dimer atoms leads to a swinging character for the phonon frequency of 5.87 THz. The flat branch at 6.33 THz along both symmetry directions is due to the opposing motion of first-layer dimer atoms in the dimer bond direction. The phonon mode at 7.13 THz includes a rotational character between a fourfold coordinated Ga atom in the second layer and its two neighboring As atoms. Finally, we have observed that phonon modes with higher frequencies are related to the vibrations of dimer atoms and threefold Ga atoms with components in both [010] and [001] directions.

Now, we analyze the vibrational character of some significant surface phonon modes at the $\bar{J}$ point. In the phonon dispersion along the $\bar{\Gamma}$-$\bar{J}$ direction, we observe that both the Rayleigh wave (RW) and second acoustic branch lie below the projected bulk band for large **q** vectors. The atomic displacements of these acoustic phonon modes and some interesting surface optical phonon modes are displayed in Fig. 4. The RW frequency is characterized by vibrations of dimer atoms, threefold and fourfold coordinated Ga atoms perpendicular to the **q** wave vector in the surface normal direction. This result clearly indicates that this phonon mode has a transverse acoustic character, while the second acoustic frequency is a longitudinal mode due to the vibrations of surface atoms parallel to the **q** wave vector direction. The lowest surface optical frequency at 1.94 THz is related to the nearly flat branch along the $\bar{\Gamma}$-$\bar{J}$ direction. We have observed five phonon modes with a rocking character of first-layer atoms. The frequencies of these phonon modes are 3.52,

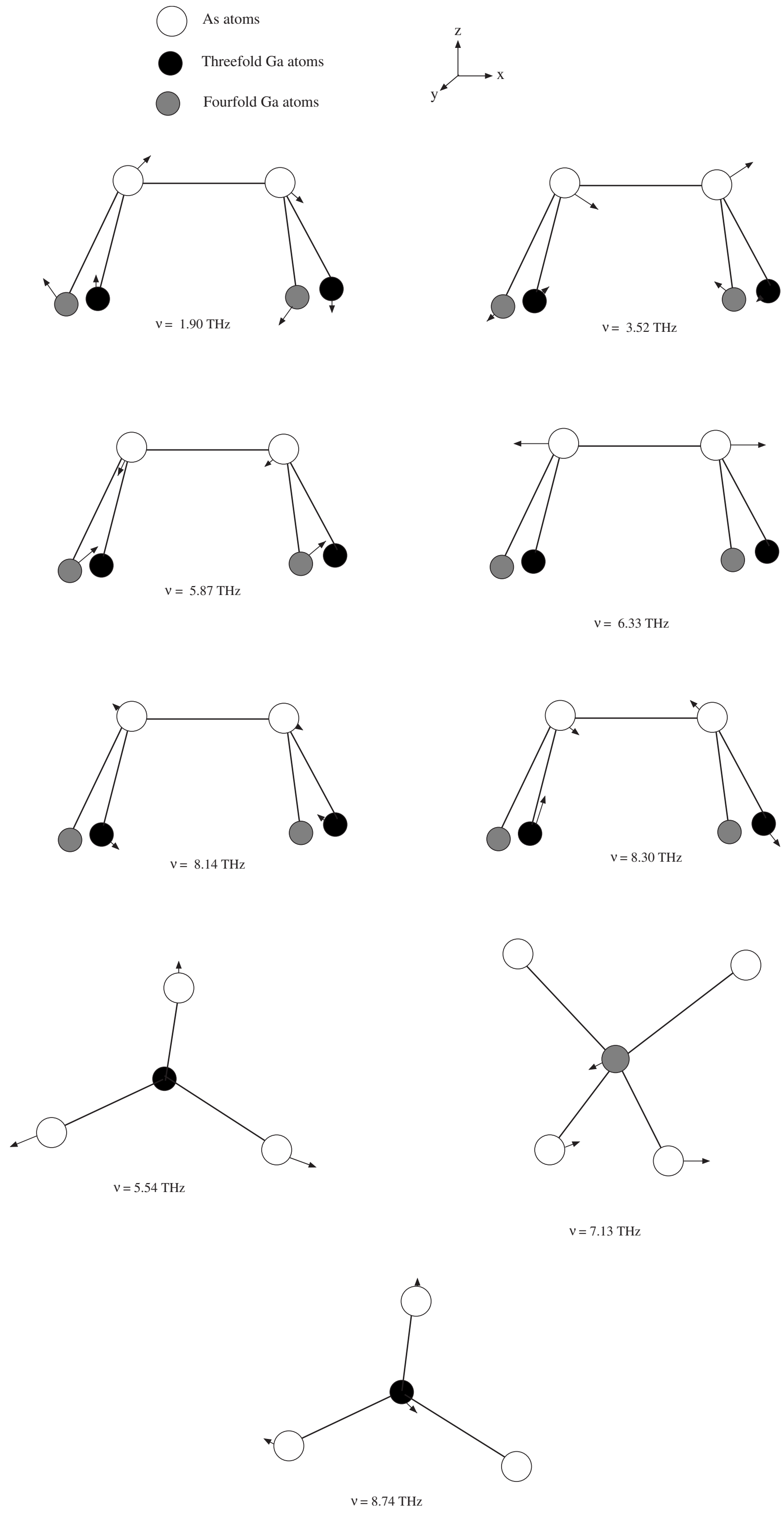

FIG. 3. Schematic representation of the displacement patterns of zone-center *ab initio* phonon modes.

3.65, 5.18, 6.19, and 8.12 THz. These phonon modes can be separated in three groups according to the atomic vibrations of threefold or fourfold Ga atoms. The first three of these include atomic vibrations from all Ga atoms. The phonon mode at 6.19 THz includes atomic vibrations only from fourfold Ga atoms, while only threefold Ga atoms move for the phonon mode at 8.12 THz. The frequency of the highest optical branch is found to be 8.72 THz at this $\mathbf{q}$ point. In agreement with the corresponding zone-center phonon mode, this mode includes atomic vibrations from threefold Ga atoms.

Figure 5 presents the calculated surface phonon frequencies and their atomic displacement patterns for some modes at the $\overline{J'}$ point. Two surface acoustic modes are found along the $\overline{\Gamma}$-$\overline{J'}$ direction, which strongly mix with bulk states. The zone boundary energies of these phonon modes are found to be 1.38 and 1.54 THz. Other phonon modes can be separated

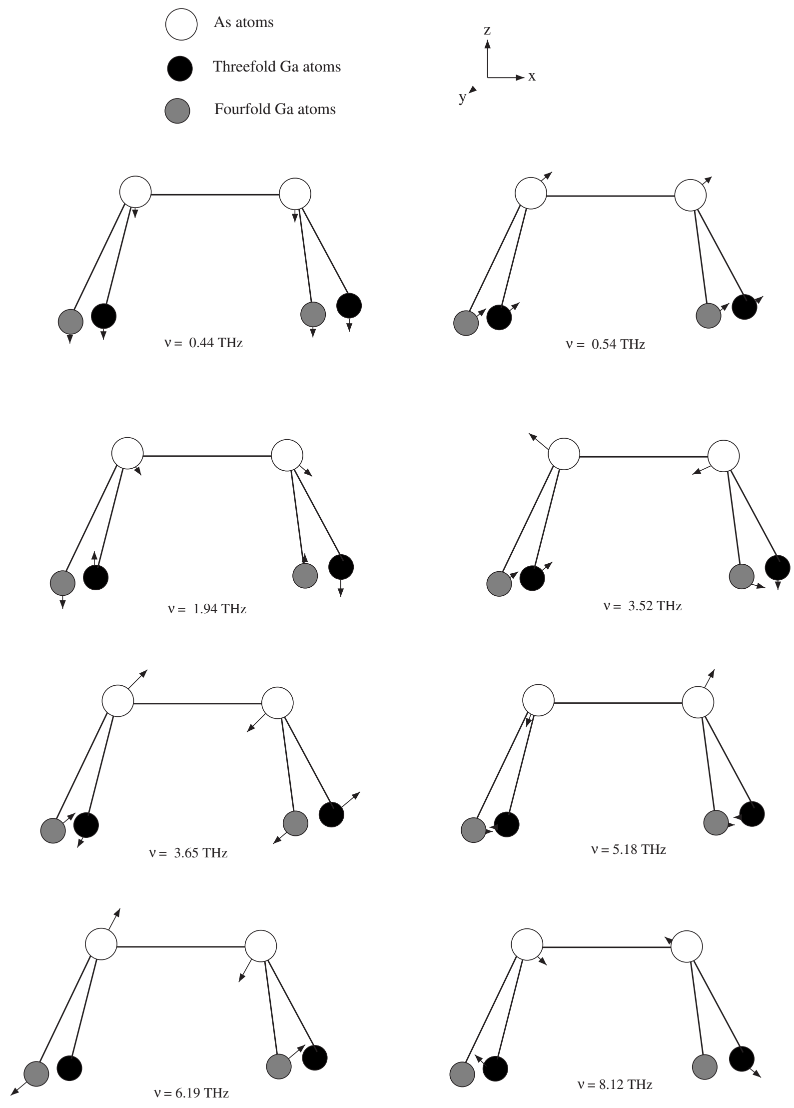

FIG. 4. Eigenvector representations of some of the phonon modes for the GaAs(001)-$\beta_2(2\times4)$ surface at the $\bar{J}$ point.

into two groups according to the vibrations of Ga atoms. The phonon modes at 2.28, 6.11, and 6.48 THz include atomic vibrations from the fourfold coordinated Ga atoms, while threefold coordinated Ga atoms vibrate for phonon modes with energies of 3.52, 8.12, 8.31, 8.40, and 8.52 THz. In particular, the phonon mode at 6.11 THz has a rotational character due to the opposing motion of As dimer atoms.

2. Bond-charge model phonon results

We have plotted our BCM results, together with our *ab initio* results, in Fig. 6. In general, the results from both calculations are in reasonably good agreement with each other. The right hand panel of Fig. 6 shows the surface DOS obtained from the BCM and its comparison with the corresponding bulk results. In agreement with the *ab initio* work, this method produces surface peaks in the frequency range 3.5–5 THz, where there are no bulk peaks. At around 5.5 THz, the bulk peak has been enhanced by resonant surface features. There is a clear surface peak at around 6 THz. In the frequency range 7–8.5 THz, there are two huge surface peaks, which include a large bulk contribution. In the left hand panel of this figure, we have compared the DOS results from the BCM and *ab initio* calculations. In the frequency range 3–5.5 THz, the two methods produce similar number and amplitude of peaks. However, the *ab initio* peak at 4.2 THz has shifted down by 0.5 THz in the BCM result. Similarly, the *ab initio* peak at around 5 THz has shifted upward by 0.5 THz in the BCM result. Such differences can be expected to arise from different theoretical methods and are within margins of experimental measurements. Both methods predict surface peaks at around 6 and 7 THz. The biggest difference in the DOS from the two methods lies in the location and amplitude of the highest peak. The *ab initio* method predicts a shoulder at around 8.5 THz. The BCM, on the other hand, predicts a huge peak at around 8.5 THz. This difference in the BCM and *ab initio* results is partly rooted in the difference in the bulk DOS in that frequency region and partly in the simplicity of the treatment of surface effects within the BCM.

Some calculated zone-center phonon frequencies from the BCM calculations are compared with our *ab initio* calculations in Table I. The comparison in this table has been made according to atomic displacement patterns and energy loca-

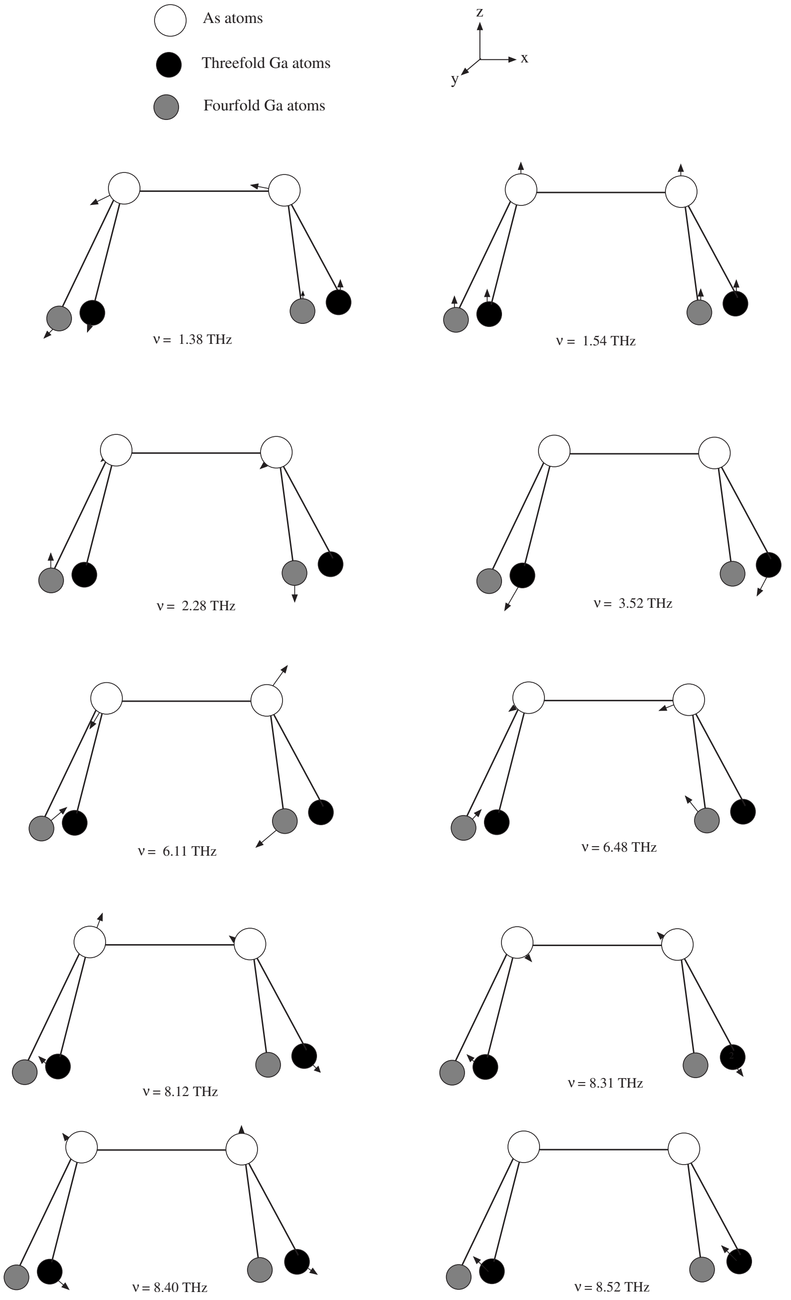

FIG. 5. Eigenvector representations of some of the phonon modes for the GaAs(001)-$\beta_2(2\times4)$ surface at the $\overline{J'}$ point.

tions of surface phonon modes from both calculations. Special phonon modes, such as rocking and dimer stretch modes, have also been observed in the BCM work, with energies of 3.02 and 5.67 THz, respectively. These modes are in good agreement with the corresponding *ab initio* values of 3.52 and 6.33 THz. However, we have identified two differences between the surface results obtained from the two theoretical models in this work. Firstly, in our BCM work, we are unable to identify the third-layer dimer rocking mode, which was determined at 3.63 THz obtained from our *ab initio* calculations. The second difference is related to the atomic displacement pattern of the highest surface optical phonon mode. Our *ab initio* calculations indicate that this phonon mode includes atomic vibrations from threefold Ga atoms. However, using the BCM model, we have observed that fourfold Ga atoms vibrate for this mode.

In agreement with our *ab initio* calculations, the surface acoustic modes obtained from the BCM work fall below the bulk continuum close to the zone edge point of $\bar{J}$ along the $\bar{\Gamma}$-$\bar{J}$ direction. At the $\bar{J}$ point, the frequencies of these branches are found to be 0.40 and 0.56 THz, which are in excellent agreement with their corresponding *ab initio* values of 0.44 and 0.54 THz. At this **q** point, a comparison of the BCM and *ab initio* results for the GaAs(001)-β_2 (2×4) surface are given in Table I. Our BCM calculations predict a rocking mode at 3.58 THz, which comes from the opposing motion of first-layer dimer atoms. Our BCM frequency at 5.10 THz can be compared with our *ab initio* frequency at 5.18 THz. However, in contrast to the *ab initio* calculations, our BCM calculations suggest that fourfold Ga atoms move along the surface normal direction with large atomic vibra-

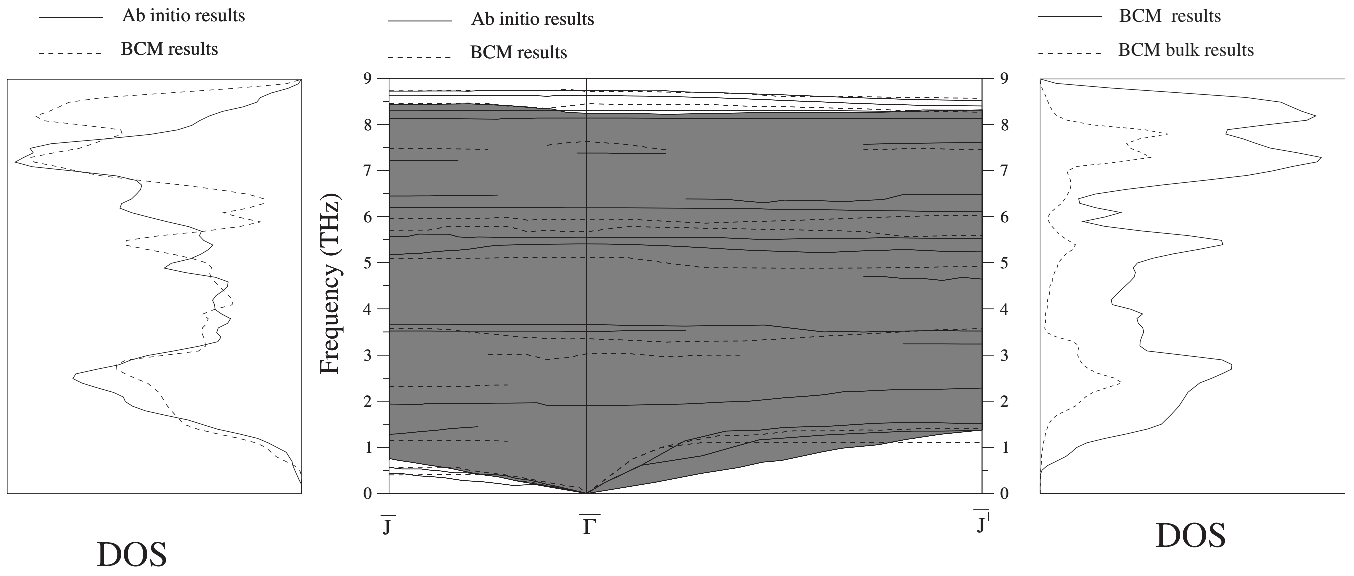

FIG. 6. Comparison of the phonon modes obtained from the *ab initio* and BCM calculations for the GaAs(001)-$\beta_2(2\times4)$ surface. The left hand panel shows the surface DOS results from the BCM and *ab initio* calculations. The right hand panel compares the bulk and surface DOSs, obtained from the BCM calculations.

tions for this phonon mode. Another difference has been observed between the BCM mode at 5.99 THz and the *ab initio* mode at 6.19 THz. Figure 4 clearly shows that fourfold Ga atoms vibrate for the *ab initio* phonon mode at 6.19 THz, while the BCM phonon mode at 5.99 THz includes large atomic vibrations from threefold Ga atoms along the dimer direction. Finally, the highest optical BCM mode is dominated by the opposing motion of the fourfold Ga atom and its neighboring As atom in the surface normal direction.

Along the $\bar{\Gamma}$-$\overline{J'}$ direction, we have not observed a flat branch with a frequency of 2.3 THz in our BCM calculations. This is the main difference between both models along this symmetry direction. Notwithstanding this difference, the results from both models, which are shown in Table I, agree with each other at the zone edge point of $\overline{J'}$. At this **q** point, the BCM surface acoustic modes lie at slightly smaller frequencies than their counterparts in our *ab initio* calculations. Once again, the differences between surface phonon modes from the two models are related to the atomic vibrations of threefold and fourfold Ga atoms. The BCM phonon mode at 6.02 THz includes atomic vibrations from threefold Ga atoms, while Fig. 5 clearly shows that these atoms do not vibrate for the corresponding *ab initio* phonon mode at 6.11 THz. An opposite situation has been observed for the BCM phonon modes at 8.26 and 8.57 THz. In contrast to their corresponding *ab initio* phonon modes, these BCM modes include atomic vibrations from fourfold Ga atoms.

We believe that the above discussed differences in the surface modes from the two theoretical models mainly arise due to the lack of a proper treatment within the BCM work of the role played by threefold coordinated Ga atoms. We further believe that in such an intricate case, it is necessary to apply a more sophisticated theoretical method, in particular, a method which treats interatomic force constants at heavily reconstructed surfaces, such as GaAs(001)-$\beta_2(2\times4)$, by

TABLE I. Phonon frequencies on the GaAs(001)-$\beta_2(2\times4)$ surface from the *ab initio* and the BCM calculations.

					Frequencies (THz)				
					Γ point				
BCM			3.02		5.11	5.67	7.60	8.30	8.70
ab initio			3.52	3.63	5.87	6.33	7.13	8.46	8.74
					$\bar{J}$ point				
BCM		0.40	0.56	2.32	3.58	5.10	5.99	8.45	8.74
ab initio		0.44	0.54	1.94	3.52	5.18	6.19	8.31	8.72
					$\overline{J'}$ point				
BCM	1.10	1.40		3.57	4.91	5.59	6.02	8.26	8.57
ab initio	1.38	1.54	2.28	3.52	5.23	5.53	6.11	8.31	8.52

considering the role of surface electronic states in a more comprehensive manner. The results obtained from the presently employed *ab initio* method are thus to be taken as superior over the BCM results.

It is physically intuitive to appreciate that the picture of a "local" phonon mode derived from the threefold Ga atoms obtained from the *ab initio* work matches with the previously known result that the lowest unoccupied electronic state on this surface also originates from the threefold Ga atoms. Indeed, it is the presence of threefold Ga atoms that presents the fingerprint of the reactivity of the GaAs(001)-$\beta_2(2\times4)$ surface. In other words, adsorption of atoms or molecules on this surface is most likely to take place via their interaction (or chemisorption) with the threefold Ga atoms. This suggestion is supported by the interpretation by Eggeling *et al.*[17] that the Ga-H modes are more intense than the As-H modes on the Ga-rich GaAs(001)-$c(8\times2)$ surface.

IV. SUMMARY

Results of structural properties of the GaAs(001)-$\beta_2(2\times4)$ surface, using *ab initio* density-functional theory, have been presented and discussed. Our structural parameters are in good agreement with previous theoretical calculations. Using our relaxed atomic geometry, calculations of the surface phonon modes on this surface have been performed by employing two different methods: *ab initio* pseudopotential method within the local density-functional perturbation scheme and an empirical adiabatic bond-charge model. In general, surface phonon results from both models agree with each other. Both theoretical models have predicted dimer rocking and dimer stretch phonon modes with frequencies of around 3.5 and 6.0 THz. We have also found that the highest surface optical phonon branch lies above the bulk continuum, while surface acoustic branches lie below the bulk continuum close to the zone edge along the $\bar{\Gamma}$-$\bar{J}$ direction.

Although surface phonon frequencies from both methods are in good agreement with each other, two differences have been observed in the results obtained from the two methods. Firstly, the BCM work did not predict the rocking mode which was determined at 3.63 THz obtained from the *ab initio* calculations. Secondly, there is some difference in the atomic displacement patterns of surface phonon modes with higher frequencies. In particular, our *ab initio* work suggested that the highest surface optical phonon mode includes atomic vibrations from threefold Ga atoms, while the corresponding BCM mode is characterized by atomic vibrations of fourfold Ga atoms. It is argued that these differences may be rooted in the empirical nature of the adiabatic bond-charge model. The presence of the local phonon mode, together with the lowest unoccupied electronic state, arising from threefold Ga atom strongly suggests that surface reaction is most likely to initiate at such Ga atoms.

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