Atomic vibrational modes on GaAs(001)-$\beta_2(2\times4)$

H. M. Tütüncü* and G. P. Srivastava
School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, United Kingdom
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Atomic vibrational modes on the GaAs(001)-$\beta_2(2\times4)$ surface have been determined by applying a combination of the *ab initio* plane-wave pseudopotential method and a linear response scheme. It is found that the highest surface frequency mode lies at 8.74 THz and originates from the threefold coordinated Ga atom in the subsurface layer vibrating against its neighboring As atoms in the top and third layers. The As-As dimer stretch mode is found to lie at 6.33 THz. Energy locations and polarization characteristics of As-As dimer rocking and swinging phonon modes have also been identified and discussed.

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Surface vibrational property is of fundamental importance and is directly related to understanding of reconstructions, phase transitions, and chemical reactions. One of the most studied semiconductor surfaces is GaAs(001), primarily because of its importance in the growth process of electronic and optoelectronic devices. In particular, the stability of the As-terminated GaAs(001)-$\beta_2(2\times4)$, with 0.75 monolayer coverage of As, has been extensively verified. The atomic geometry and electronic structure of this surface have been thoroughly studied, both experimentally[1,2] and theoretically.[3–5]

The accepted geometry of the GaAs(001)-$\beta_2(2\times4)$ surface is characterized by two As dimers and two missing As dimers on the top layer, missing Ga atoms in the second layer beneath the two missing As dimers, and one As dimer in the exposed third layer.[3] The Ga atoms in the second layer experience two types of local bonding configuration: Ga atoms lying along the center line of the top-layer As dimer block are fourfold coordinated and the Ga atoms at the edge of the dimer block are threefold coordinated. This leads to a bimodal Ga-As bond length distribution between the top and second layers.[4] The highest and second-highest occupied surface electronic states have a π^* character, localized at the third-layer and top-layer As dimers, respectively.[5,6] The energies of these states are very close to each other. The lowest unoccupied surface electronic state is due to the dangling bonds of the threefold second-layer Ga atoms.[6]

Surface phonons have been investigated by means of inelastic particle-scattering techniques such as high resolution electron energy loss spectroscopy (HREELS) and helium atom scattering (HAS), and by means of optical spectroscopic techniques such as Raman scattering, infrared absorption, and time-resolved second-harmonic generation (TRSHG). For example, phonon modes on H-GaAs(001)-$c(8\times2)$ have been investigated by HREELS.[7] The TRSHG technique has been extensively applied for measurement of phonon modes on the Ga-rich GaAs(001) surface[8] with reconstructions (1×6), (4×6), and (4×1). The current study is of phonon modes on As-rich GaAs(001) surfaces. Knowledge of surface phonon modes on the As-rich GaAs(001)-$\beta_2(2\times4)$ would serve important purpose. It would be of interest to determine the energy location and eigenmode of the highest surface phonon mode. In particular, the threefold coordinated Ga atoms on this surface are undercoordinated and are thus reactive atomic species and can also play an important role in surface passivation. Identification of phonon modes related to such Ga atoms is therefore of high significance.

In this work we present results for zone-center surface phonon modes of the GaAs(001)-$\beta_2(2\times4)$ surface by employing *ab initio* theoretical technique, the density functional scheme, and a linear response method. In particular, we have examined the modes arising from vibrations involving the threefold Ga atoms in the subsurface layer and the As dimer atoms in the top and third layers.

We first calculated the relaxed geometry and the corresponding electronic states for the surface by using the density functional theory in its local density approximation within a supercell modeling scheme. We treated the electron-electron exchange and correlation interactions within the Kohn-Sham[9] and Perdew-Zunger[10] schemes, respectively. Ion-electron interactions were treated by using norm-conserving pseudopotentials.[11] Single-particle wave functions were expanded in a plane-wave basis set up to 15 Ry kinetic energy cutoff. The electronic charge density was evaluated by employing four special **k** points within the irreducible part of the Brillouin zone. The results for the atomic geometry and electronic states were used to calculate zone-center phonon modes by employing the code PWSCF which is based on the application of the density functional perturbation theory (see Ref. 12).

The main features obtained in this work for the relaxed atomic geometry on the surface are consistent with previous and similar calculations (see, e.g., Refs. 5 and 6). In particular, as shown in Fig. 1, the bond 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. These values are in agreement with experimentally determined results obtained by Garreau *et al.*[13] There is a vertical buckling of about 0.26 Å between the threefold and fourfold coordinated Ga atoms in the second layer, with threefold Ga atoms lying lower. The bond length between threefold coordinated Ga (in the second layer) 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 fourfold coordinated Ga (in the

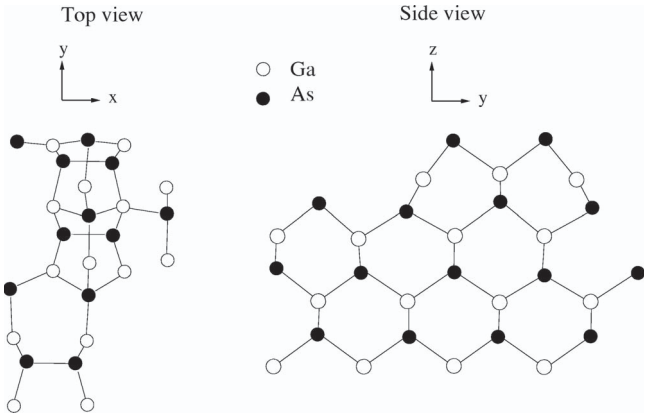

FIG. 1. Top and side views of the relaxed atomic geometry of the GaAs(001)-$\beta_2(2\times4)$ surface.

second layer) and its As neighbors in the top layer. In agreement with previous work (e.g., Ref. 6), the two closely lying highest occupied surface electronic state are found 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.

A number of surface phonon modes at the center of the surface Brillouin zone have been identified. Energies of all but one such modes lie within the bulk phonon spectrum. The highest surface-localized phonon mode lies at 8.74 THz, slightly above the bulk LO frequency of 8.50 THz. This mode results from vibrations of the threefold Ga atoms (in the second atomic layer) against their neighbors (in the top and third atomic layers). As indicated in Fig. 2, all the three atoms vibrate in the plane normal to the As-As dimer line. The third-layer As neighbor vibrates against Ga (both with almost equal amplitude) along the Ga-As bond direction, and the top-layer As vibrates with a smaller amplitude along the surface normal. Upon adsorption of atoms or molecules on the surface it is this "local" mode that is most likely to be "quenched," thus proving a highly significant signal for the onset of surface passivation or surface reaction.

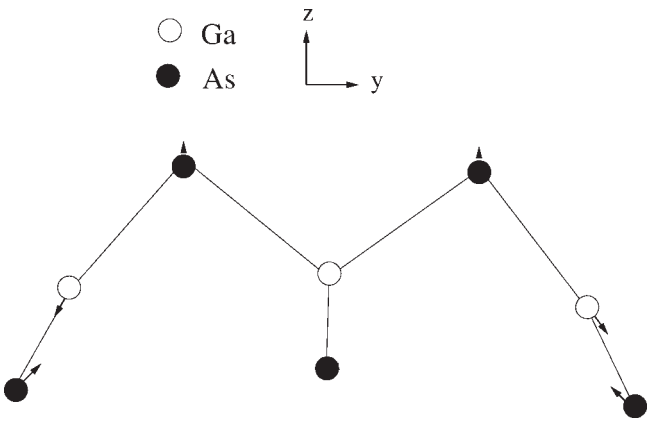

FIG. 2. Atomic vibrational pattern corresponding to the highest surface vibrational mode at 8.74 THz on the GaAs(001)-$\beta_2(2\times4)$ surface.

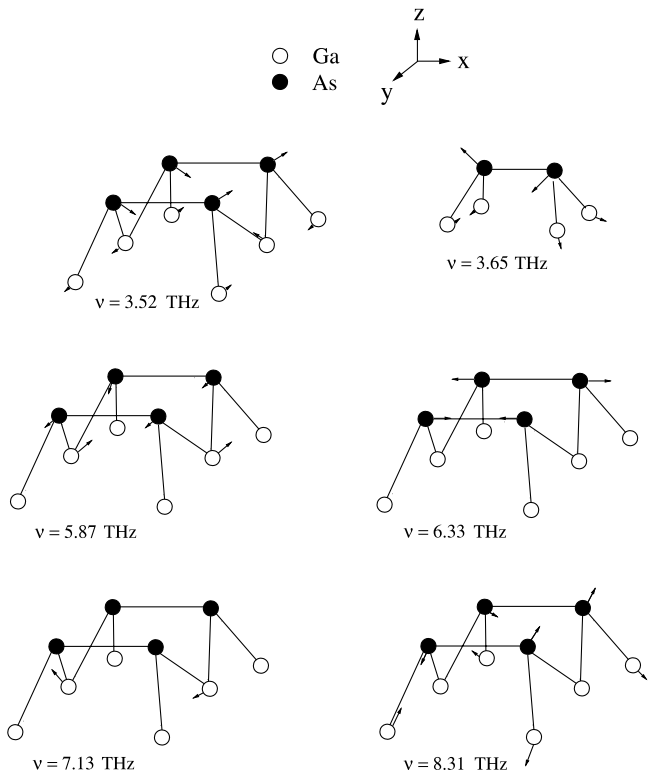

FIG. 3. Eigenvector representations of a few more interesting phonon modes on the GaAs(001)-$\beta_2(2\times4)$ surface.

In addition to the local surface mode, we have identified six other surface phonon modes at 3.52, 3.65, 5.87, 6.33, 7.13, and 8.31 THz within the bulk spectrum. The eigenvectors representations of these phonon modes are shown in Fig. 3. Among interesting phonon modes are two dimer rocking phonon modes. The rocking mode due to the two top-layer dimers lies at 3.52 THz. The rocking mode due to the third-layer dimer lies at 3.65 THz. The effective surface dipole can be expected to be strongly modulated by these surface rocking mode vibrations. The surface vibration at 5.87 THz shows a swinging character of dimer atoms. For this mode, the top-layer dimer block vibrates against the Ga atoms underneath (fourfold coordinated Ga atoms in the second layer). The mode at 6.33 THz has dimer stretch character. We have clearly identified this mode for the top-layer dimers. Although the atomic masses of Ga and As atoms are rather similar, as the As-As dimer length is much larger (and hence weaker) than the Ga(threefold)-As bond length, the dimer stretch vibrational mode occurs at a smaller frequency than the localized surface Ga-As mode. The fourfold Ga atoms underneath the dimer block vibrate against their fourth-layer As neighbors to produce the mode at 7.13 THz. The mode at 8.31 THz can be considered as another type of rocking mode, in which the top-layer dimer block vibrates against the threefold coordinated Ga atoms in the second layer. Although there are no reports of phonon mode measurements on the GaAs(001)-$\beta_2(2\times4)$ surface, we note that up to four phonon modes have been identified in the frequency range 6–8 THz by TRSHG measurements on As-rich GaAs(001)-(1×6) and Ga-rich GaAs(001)-(4×1) surfaces.[8] Due to different surface geometries, the modes on these surfaces are proposed to

have different polarization characteristics than we have obtained for the GaAs(001)-$\beta_2(2\times4)$ surface.

In summary, first-principles calculations have been carried out for surface vibrational modes on the GaAs(001)-$\beta_2(2\times4)$ surface. Seven significant modes have been identified and their energy locations and polarization characteristics explained. The frequency of the As-As dimer stretch mode lies below the mode involving the threefold Ga and its neighboring As atoms. It is argued that upon adsorption of elemental or molecular species, the most likely change in the surface vibrational pattern is expected to be in two optical modes involving threefold Ga and their neighboring As atoms, with frequencies (8.31 THz and 8.74 THz) close to the highest bulk longitudinal mode. It is hoped that the results presented here will help the determination and monitoring of phonon modes on this surface using experimental techniques such as HREELS and TRSHG.

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*Permanent address: Sakarya Üniversitesi, Fen-Edebiyat Fakültesi, Fizik Bölümü, Mithatpasa, 54100, Adapazarı Turkey.

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