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Theoretical Study of the Surface Optical Properties of Clean and Hydrogenated GaAs(110)

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We present a calculation of the electronic and optical properties of the GaAs(110):H surface performed within the first-principles density functional theory (DFT) in the local density approximation (LDA). The geometry and electronic structure are analyzed and compared with those of the clean surface. The reflectance anisotropy spectrum and the differential reflectivity are then computed. Taking into account the usual underestimation of the LDA gaps with respect to the experimental values, the comparison between our theoretical spectra with available experimental reflectance data shows a satisfactory agreement, allowing for the interpretation of the main structures in terms of electronic transitions.

1. Introduction

Optical spectroscopies have lately been more and more involved in experimental in-situ surface studies because they are non-damaging, allow to study surfaces also under non-ultrahigh vacuum conditions and are sufficiently fast to follow surface modifications in real time. Especially the reflectance anisotropy spectroscopy (RAS), measuring the anisotropy with respect to light polarisation, has shown excellent surface sensitivity. RAS measures the difference of reflectivity when normal incident light, polarized along two orthogonal directions x , y , is used. It is hence defined as:

$$\frac{\Delta R}{R} = \frac{R_y - R_x}{R} \quad (1)$$

with R being the reflectivity for nonpolarized light. If the bulk of the material under investigation is optically isotropic, as it is if the structure is cubic, then any non-vanishing signal of the RAS is due to surface effects: the RAS signal is a probe of the surface. Another optical technique used to study surfaces is the differential reflectivity spectroscopy (SDR). This technique has been introduced by Chiarotti and coworkers in 1968 (for a review see [1]), and gave the first direct evidence of surface electronic states by purely optical means. SDR is based on the difference of the reflectivity of the clean surface and the passivated surface. Passivation can be obtained for example by oxigena-

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tion or hydrogenation of the surface. The SDR signal is defined as

$$\text{SDR} = \frac{R_{\text{clean}} - R_{\text{pass}}}{R_{\text{clean}}} \quad (2)$$

and gives the contributions to the reflectivity of those surface states that have been removed through passivation.

We present here a study of both the reflectance anisotropy and Differential reflectivity of GaAs(110). This surface is well known from an experimental point of view, the electronic and optical properties have been measured [2 to 4] and calculated [5 to 8]. For what concerns the hydrogenated surface, much less is known. Energy loss [9, 10] and photoemission [11] have given indications on the disappearance of the clean surface states and the appearance of new surface states with H dosage. Hydrogenation has been used as a means to passivate the surface dangling bonds by Chiaradia and coworkers [12] in order to study, through the SDR, the surface states of the clean GaAs(110) surface. A study of the H covered surface has been also carried out by Cardona and coworkers [13]. Theoretical calculations of the geometry have been done with ab-initio methods by Bertoni and colleagues [14], whereas optical properties calculations are limited to the semiempirical pseudopotential approach [6]. Here, we calculate the geometry, the electronic and optical properties of the GaAs(110):H surface within a first principles approach.

2. Method

Our calculations are carried out within the density functional theory in the local density approximation (DFT-LDA) [15]. The atomic positions of the relaxed surface (clean and hydrogenated) are determined by using the Car-Parrinello molecular dynamics approach [16]. We use norm-conserving pseudopotentials [17, 18]; nonlinear core corrections [19] for Gallium are included. The single electron states are expanded in a set of plane waves corresponding to a cutoff of 18 Ry. We have used four special k-points in the irreducible part of the Brillouin zone (IBZ) for the determination of the equilibrium geometry, whereas 64 special k-points in the IBZ are used for the calculation of the optical properties.

2.1 Geometry

The calculated bulk lattice constant is 5.61 Å, in good agreement with the experimental value of 5.65 Å. The clean surface is characterized by an upward relaxation of As atoms whereas Ga atoms move inwards. A sketch of the surface structure is given in Fig. 1a. The buckling Δ_1 is 0.68 Å, in good agreement with experiments and with other ab initio calculations [5]. After hydrogen deposition, on the other hand, there is a counterrelaxation: the As atoms move inwards, and the Ga atoms go back to almost the ideal terminated surface position (Fig. 1b). The buckling between Ga and As is very small ($\delta_1 = 0.18$ Å), the one between H atoms is slightly larger ($\delta_h = 0.24$ Å). The Ga–H bond length is 1.57 Å, the As–H one is 1.54 Å, to be compared respectively with the values 1.59 and 1.52 Å measured in molecules.

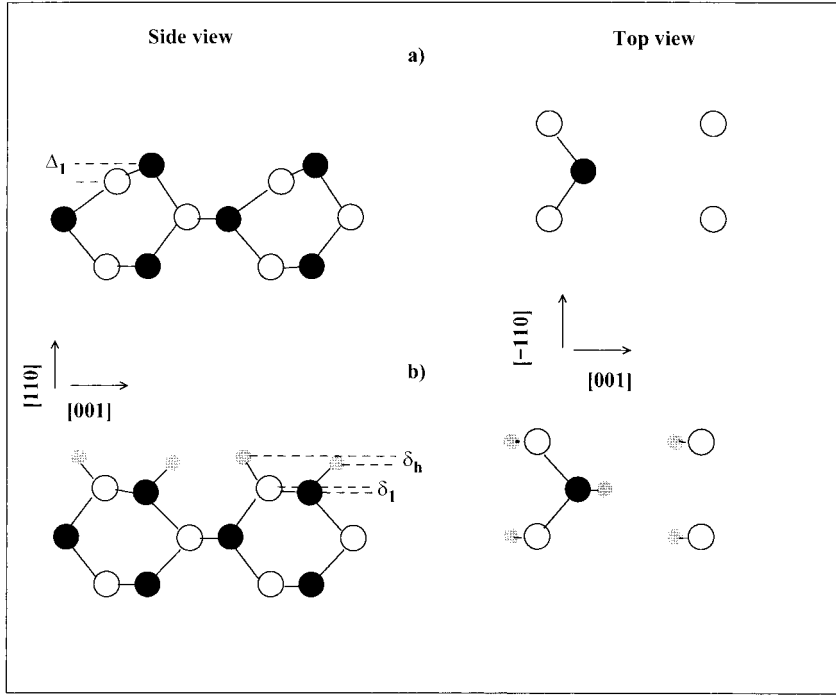


Fig. 1. a) Calculated geometries of a) the GaAs(110) and b) the GaAs(110):H surface. Open circles: Ga atoms; black circles: As atoms; gray circles: H atoms. $\Delta_1 = 0.68 \text{ \AA}$; $\delta_1 = 0.18 \text{ \AA}$; $\delta_h = 0.24 \text{ \AA}$

2.2 Band structure

The slab band structures for the clean and hydrogenated surfaces are shown in Fig. 2a, b. The surface states are indicated by black large circles, the dots correspond to bulk states. In Fig. 2a the cation band C_3 is related to the gallium empty dangling bond. The band A_5 is instead related to the filled dangling bonds of arsenic. After hydrogen deposition, the dangling bonds are saturated, and the corresponding electronic states are pulled apart and shifted away from the gap region (Fig. 2b). In agreement with previous ab-initio calculations [14], the gap region becomes empty of surface states and H-related states. Also the surface bands A_2 , C_2 and A_3 disappear after hydrogenation, and two new surface bands appear, one in the stomach gap and one about 11 eV below the top of the valence band. Weak resonances are also seen both in the valence and in the conduction bands.

2.3 Optical results

Growing one monolayer of hydrogen in a controlled way is very difficult from an experimental point of view, because H atoms usually cause etching of the surface and create defects. For this reason, good quality H-covered surfaces are very difficult to obtain; as a consequence, experimental data are rare, and the results are strongly dependent on the preparation conditions. Experimental RAS spectrum of the GaAs:H

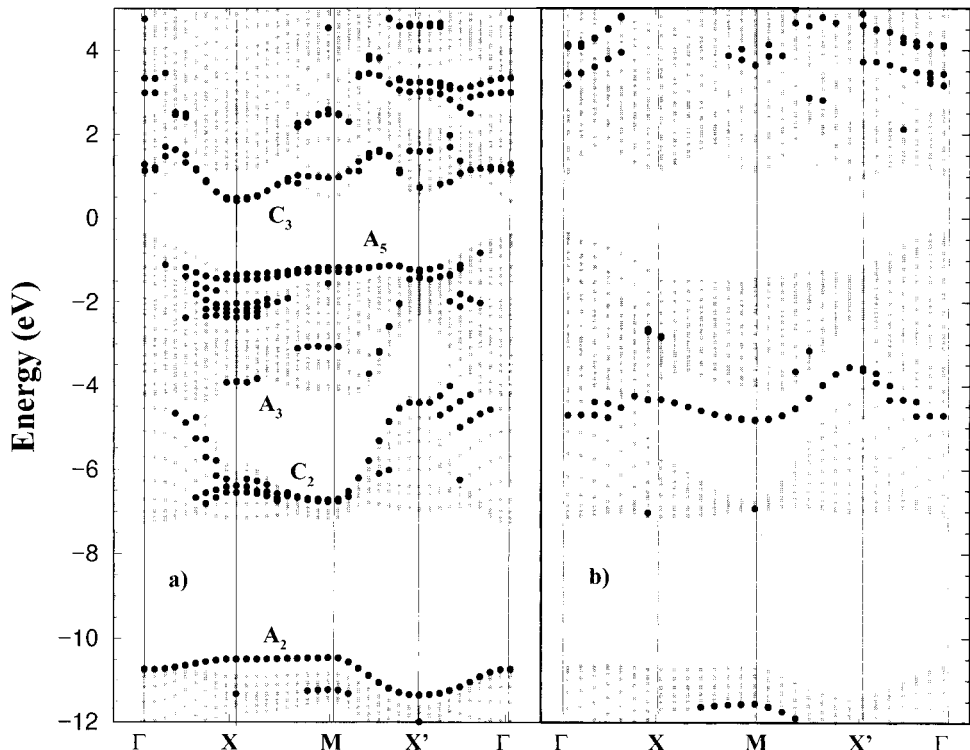


Fig. 2. Calculated DFT-LDA band structure for a) the clean and b) the hydrogenated GaAs(110) surface. Large dots represent surface states, small dots bulk states

surface [13] is shown in Fig. 3d together with the results for the clean surface [4] (Fig. 3b). Our RA spectra, calculated according to Eq. (1), are also shown (Fig. 3a, c). The RAS of the clean surface has been calculated including many-body effects within the GW approximation [8]; the one of the hydrogenated surface, instead, is calculated within DFT-LDA and a scissor operator of 0.7 eV has been used. Concerning the clean surface, at 2.7 eV we find a pure surface-state peak (due to transitions across surface states around the \bar{X} point of the two-dimensional BZ), whereas the main optical structures at higher energies are due to surface-perturbed bulk states at the high symmetry points of the BZ; the dip at about 3.2 eV and the subsequent peak correspond to the E_1 bulk structure; the next peak at about 4.3 eV corresponds to the E'_0 structure; the dip at 4.7 eV is the E_2 structure, due to bulk transitions at the X point of the bulk BZ. Further details for the clean surface are given in Ref. [8].

The anisotropy of the hydrogenated surface, on the other hand, turns out to be exclusively generated by bulk states perturbed by the surface. No surface state is involved in the energy range considered. The strong peak around 3 eV and the subsequent one at 3.4 eV are mainly due to bulk transitions along the $\bar{\Gamma} - \bar{X}'$ direction.

The knowledge of the reflectivity of both the clean and hydrogenated surface allows to determine the differential reflectivity (SDR) (see Eq. (2)). This is shown in Fig. 4, together with the experimental result of [12]. A scissor operator shift of 0.7 eV has

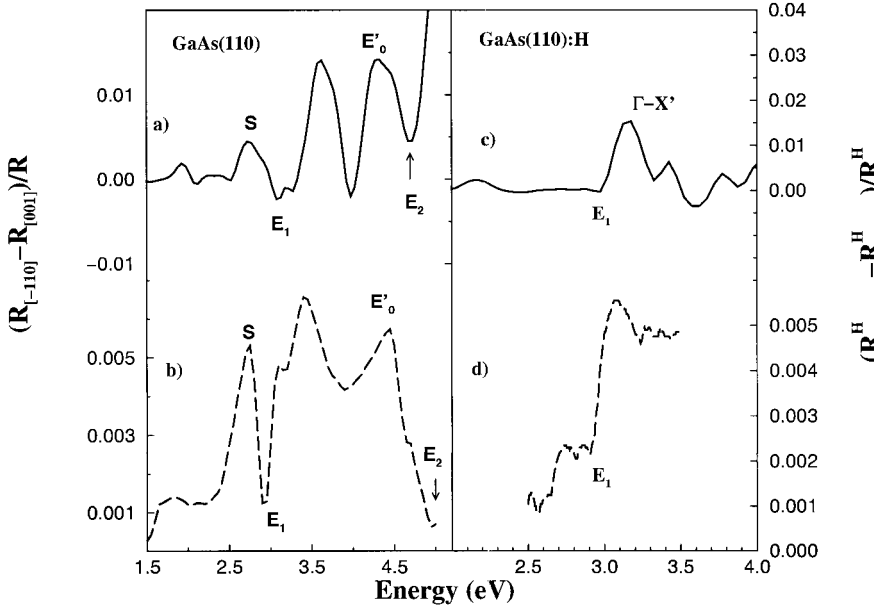


Fig. 3. Reflectance anisotropy spectra for the clean (left panel) and hydrogenated (right panel) surface: a) theoretical result and b) experimental spectrum [4] for GaAs(110); c) theoretical result and d) experimental spectrum [13] for GaAs(110):H

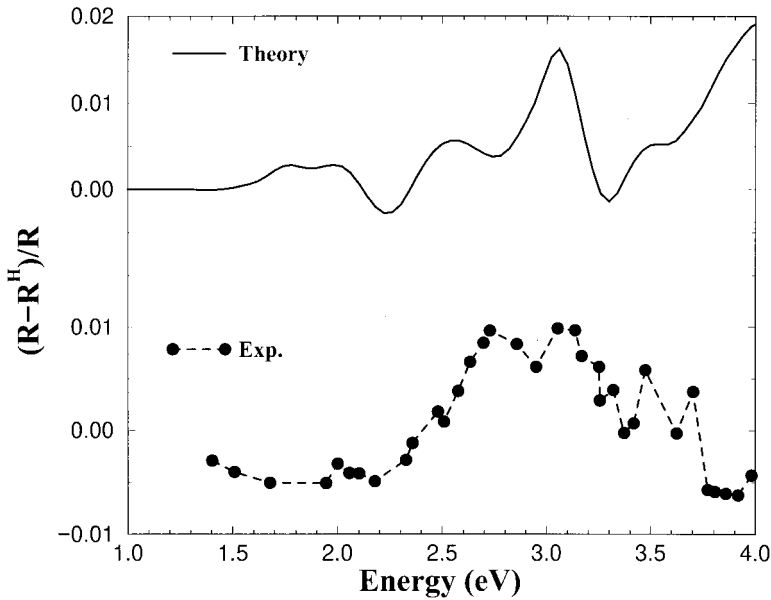


Fig. 4. Differential reflectance calculated according to Eq. (2), and experimental result of [12]

been used in the theoretical spectrum. The agreement between theory and experiment is qualitative, nevertheless it is possible to interpret the main features of the experimental spectra. The broad positive structure and the following dip between 1.5 and 2.0 eV are due to transitions at the $\bar{\Gamma}$ point of the BZ. Surface states at \bar{X} are responsible for the structure at 2.6 eV; the subsequent peak and dip seem to be related to the bulk E_1 transitions. The interpretation of the third experimental peak is not unique, since many transitions spread over the whole BZ seem to contribute.

3. Conclusions

In conclusion, we have performed an ab-initio calculation of the geometry, the electronic and optical properties of the GaAs(110) clean and hydrogenated surfaces. The hydrogenated surface is characterized by a counterrelaxation of the Ga and As atoms. No surface states are present in the main electronic gap. The reflectance anisotropy of the hydrogenated surface is dominated by transitions involving bulk states. The differential reflectivity shows contributions from surface states at the \bar{X} point of the BZ, but also bulk states perturbed by the surface give strong contributions to the spectrum.

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