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Theoretical study of the optical response of the adsorption of Sb on the GaAs(110) surface

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A theoretical study of the optical response of the adsorption of Sb atoms on the clean GaAs(110) surface is presented. The reflectance anisotropy spectroscopy (RAS) spectrum is calculated and analysed as a function of Sb-coverage. To capture some of the possible dynamical processes of Sb sub-monolayer growth, a 1×3 unit cell is considered whose equilibrium geometry has been obtained by performing an ab-initio pseudopotential calculation with the use of density functional theory within the local density approximation. The RAS is calculated via the ab-initio scheme and also by using a semiempirical tight binding formalism. Some trends in the RAS spectra are identified as the clean surface is partially covered by Sb until the one monolayer coverage is achieved.

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1 Introduction The adsorption of atoms on clean surfaces has been studied in the past [1–3]. Among the studied interfaces, Sb on clean GaAs(110) surfaces (Sb/GaAs (110)) represents a prototypical system since deposition, at room temperature, of 1 monolayer (ML) of Sb on a clean GaAs(110) surface produces a stable and ordered (1×1) structure [4–6]. Such a structure has the same symmetry as the clean (110) surface. Several atomic geometries for such a surface were proposed: the epitaxial continued layer structure (ECLS) [7], the epitaxial on top structure (EOTS), the p^3 structure [6], the epitaxial overlapping chain structure (EOCS) [8], and the dimer model [8]. Among those proposed structures, the ECLS shown in Fig. 1 is now the widely-accepted structure for the Sb/GaAs(110) surface [3, 9–12]. In this structure the adatoms ideally continue the underlying bulk structure with two three-fold coordinated Sb atoms per surface unit cell. The Sb atoms are located at sites wherein the Ga and As atoms, on the unreconstructed surface, would be. Thus the Sb atoms form the typical zigzag chain of a (110) surface, bonded to a nearly unrelaxed substrate.

Although most of the studies of the Sb/GaAs(110) surface has been done on the 1 ML Sb-covered surface, some
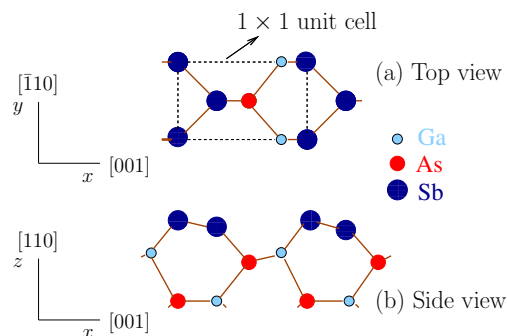
Figure 1 (Color online) Top and side views of the epitaxial continued layer structure (ECLS) of the Sb/GaAs(110) surface.

studies in the submonolayer coverage regime can be found [13–16]. Experimentally it has been found that for submonolayer coverages, Sb grows on GaAs(110) in 1-ML-high ordered patches [17–19]. In Refs. [18,19] the authors estimated, for low coverages, the density of adsorption sites of Sb. However due to the large size of the Sb clusters, even at low coverage, it was not possible for them to determine the adsorption site of the Sb on the GaAs(110) sur-

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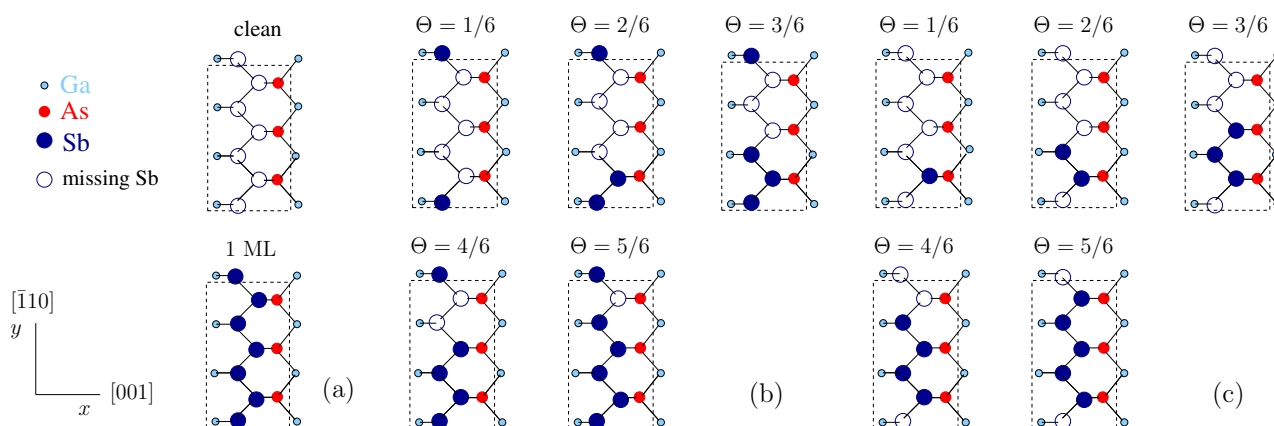
Figure 2 (Color online) Schematic top views of the considered surfaces: the clean GaAs(110) and the 1 ML Sb/GaAs(110) (panel (a)), and the partly Sb-covered GaAs(110) surfaces (panels (b) and (c)). The 1×3 unit cell is shown with dashed line and the Sb-coverage is indicated. Here the Sb atoms bond preferentially to either Ga atoms (panel b) or As atoms (panel c) (see text for discussion).

face. They claim that there is no preferential bonding to either Ga or As atoms. This is in contrast to the electron-energy-loss-epectroscopy study of Ref. [13], wherein an evidence for a preferential bonding of Sb atoms to Ga sites is found. There, the suppression of a Ga-characteristic excitonic transition was interpreted as evidence of such preferential Sb-bonding site. Ref. [15] reported a Monte Carlo model for simulating the growth of submonolayer coverages of Sb atoms on the GaAs(110) surface. It is claimed that during the first stages of the growth the Sb atoms are more stably bound to the Ga sites of the substrate rather than the As sites because of the large difference in diffusion activation energy. It is also predicted through a model that there would be a predominance of odd- over even-numbered-atom Sb chains during growth. In particular, at Sb-coverage of $\Theta = 0.2$ ML, and at a temperature of 500 K, most of Sb atoms are assembled into three-atom chains having their ends terminating on Ga atoms. For an Sb-coverage of $\Theta = 0.5$ ML, and at temperature of 500 K, there is a large number of three-atom chains, but there are also some larger odd-numbered-atom zigzag chains. A similar result has been reported in scanning tunneling microscopy studies of the growth of Ag atoms on Si(100)-2×1 surface where, in such a case, for low coverage, a predominance of even- over odd-numbered-atom Ag chains was found [20].

In this work we theoretically study the adsorption of Sb atoms on a clean GaAs(110) surface through the optical technique of RAS. This technique probes the surface and interface structure of cubic materials [1,21–30], and measures the difference between the normal-incidence optical reflectance of light polarized along the two principal axes, in the surface plane, as a function of photon energy. Since the bulk optical properties of cubic crystals are isotropic, any observed anisotropy must be related to the lower symmetry of the surface. We mainly focus on the qualitative

effects on the RAS spectra of the preferential bonding site of Sb atoms with either Ga or As atoms.

2 Theory Our model consists in taking a 1×3 unit cell of the GaAs(110) surface which is extended along the y axis ($[\bar{1}10]$ direction) as seen in Fig. 2. In order to obtain relaxed coordinates for the clean, partly Sb-covered and 1 ML GaAs surfaces, we performed a pseudopotential ab-initio calculation with the use of density functional theory (DFT) within the local density approximation (LDA). The description of the surface was done by using a supercell with 9 atomic (110) layers of GaAs and 2 Sb atoms per 1×1 unit cell in the front and back surfaces. We used a vaccum region with a thickness of 11 atomic layers. The electron-ion interaction was treated by using a relativistic separable pseudopotentials of Hartwigsen-Goedecker-Hutter (HGH) [31]. The wave functions were expanded in plane waves corresponding to a cutoff energy of 20 Ha and the Hellman-Feymann forces were less than 0.02 eV/Å. To calculate the RAS spectra we used the ab-initio method outlined above, [32] and also a semi-empirical tight binding method (SETB) within a sp^3s^* basis [33], where the relaxed coordinates are used for both. The energy and the momentum matrix elements are calculated within both approaches in the standard way and are used to evaluate the RAS spectrum [33,32], where we used 80 k-points in the irreducible part of the first Brillouin Zone for the integration of the response function. We define the RAS signal, $\mathcal{R}$, as

$$\mathcal{R} \equiv \frac{\Delta R}{R} = \frac{R_{[\bar{1}10]} - R_{[001]}}{R} \tag{1}$$

where R_i is the surface related change in the reflectivity, along $i = [\bar{1}10]$ or $[001]$ crystallographic directions, and R is the usual Fresnel reflectivity.

We mention that although we could add the ubiquitous disorder present at the surface following Ref. [33], the RAS

results are only marginally affected as long as the disorder is small, as one would expect at normal experimental temperatures. Thus, in what follows we take the atomic coordinates as obtained from the relaxation ab-initio scheme.

Since we are interested in studying a possible preferential bonding site of adatoms, we consider the formation of Sb-chains as the main process of mono-layer growth. Then, to get a particular coverage, we might consider that, on the unit cell, adatom-chains are formed in various ways. For example, the coverage of 4/6 can be formed by considering that, there is either a chain of 4 successive adatoms, or there are two adatom-chains, one with 3 adatoms and one with 1 adatom (these last two adatom-chains are separated by an empty Sb-site). In the former case, there are an equal number of adatoms that bond either to Ga or to As atoms. Whereas in the latter case, there would be more adatoms that bond to Ga atoms than to As atoms or vice versa. Thus the generated sub-monolayer surfaces have a preferential bonding site. In Fig. 2, we show the schematic top views of the considered surfaces on the present work, where the atom-positions are not the actual relaxed coordinates of the atoms. Thus, the surfaces with 4/6 (or 2/6) of Sb-coverage shown in Fig. 2(b) and Fig. 2(c) are not equivalent, i.e. they are not mirror images of each other.

3 Results In Fig. 3 we show the calculated RAS spectra for the clean GaAs(110) surface and for the 1ML - Sb/GaAs (110) surface, as well as their corresponding experimental RAS spectrum. For the clean surface we concentrate in the experimental features around the critical points of bulk GaAs, E_1 and E_2. We see that the experimental RAS signature around E_1 is a derivative-like signal, that is only qualitatively reproduced by our calculations. On the one hand, the SETB result has the right strength but it is shifted upwards in energy and the feature is less pronounced. On the other hand, the ab-initio feature has a larger strength, is shifted downward in energy, and the derivative-like feature is much more pronounced, giving a positive result for the local maximum around 2.8 eV. For the feature around E_2, we see that the SETB (ab-initio) result is blue (red) shifted, and while the SETB result overestimates the experiment the ab-initio calculation underestimates it. The ab-initio spectrum underestimates the features in between E_1 and E_2, whereas the SETB calculation gives RAS values similar to the experiment. The ab-initio result is somehow different to that reported in Ref. [34] around E_2, probably due to the different pseudopotentials used in here. For the 1ML Sb covered surface, the feature around 2.1 eV is qualitatively well reproduced by both calculations, while the position of the feature around 4.3 eV is better given by the ab-initio method than by the SETB method. In between these two energy values, the trend shown by SETB is in better agreement with the experiment, than the ab-initio results, both showing positive values as in the experiment. The rather small experimental feature around 4.8 eV is not reproduced in the calculations. Again, as for

the clean surface, the ab-initio result is somehow different to that reported in Ref. [12]. This is probably due to the different pseudopotentials used in here, that due to the large unit cell, were restricted to the HGH pseudopotentials that use valence electrons only. Including core corrections would improve the results, but the numerical burden for the large unit cells used in here, may be unsurmountable, so the qualitative agreement obtained in Fig. 3 is acceptable for the scope of the present work. Indeed, is very interesting to see how the RAS features around E_1 and E_2 change from the clean surface to the Sb covered surface, and therefore, how the RAS spectra can differentiate one surface from the other, both experimentally and theoretically.

In Figs. 4 and 5 we show the calculated SETB and ab-initio RAS spectra corresponding to the partly Sb-covered GaAs(110) surfaces schematically shown in Fig. 2, i.e. with preferential Ga or As bonding sites for the Sb atoms for coverages of $\Theta = 1/6, 2/6, 3/6, 4/6, 5/6$ ML. For the SETB results we notice that there are few differences for either of the two possible bonding sites of Sb. For $\Theta \leq 4/6$ the RAS signal is always negative, and only for $\Theta = 5/6$ the signal, particulary for the Ga bonded case, goes positive for some part of the spectra. The lower sensitivity to the bonding site shown by the SETB method could be traced back to the fact that in this scheme the interaction is restricted to nearest neighbors, and thus the overall effect of the interaction of the adsorbate with the surface may be incomplete [36]. On the other hand, the ab-initio results (Fig. 5) show clear differences between the two possible
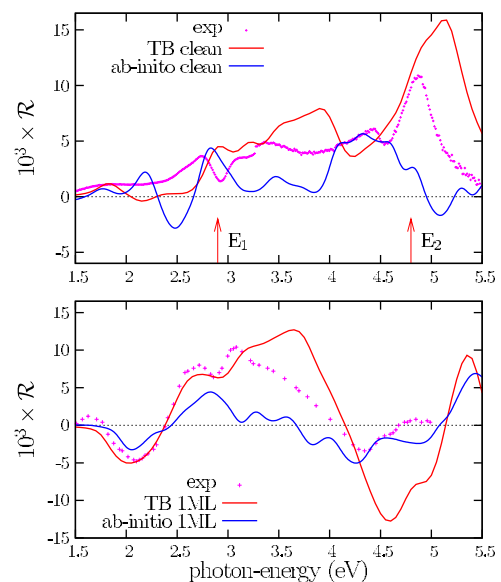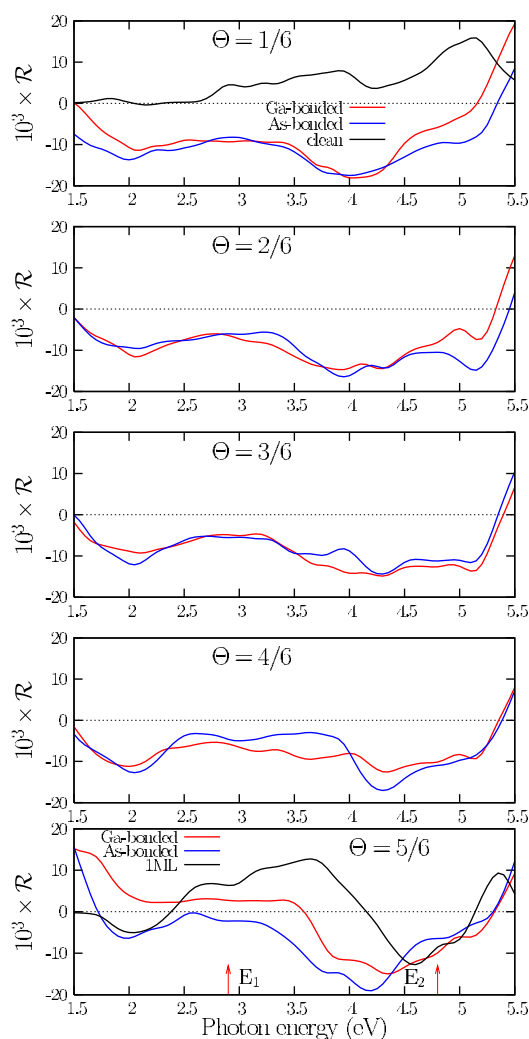

Figure 3 (Color online) RAS spectra for the clean (upper panel) and 1ML Sb covered (lower panel) GaAs(110) surfaces. The corresponding experiments are from Refs. [33] (clean) and [12,35] (1ML). The arrows show the location of the bulk critical points, E_1 and E_2, of GaAs.

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bonding sites, at least for some regions of the spectra. Indeed, for photon energies around $E_1 \sim 2.9$ eV we see that for $\Theta \le 3/6$ the Ga bonded signal is negative while for $\Theta \ge 4/6$ it is positive, while the As bonded optical response is negative for $\Theta = 1/6$ and $4/6$, and positive for $\Theta = 2/6$, $3/6$ and $5/6$. These results can be traced back to the electronic energy bands. Indeed, for any given coverage the Sb changes the morphology of the surface as it relaxes to its equilibrium position, and concomitantly the electronic states change producing optical transitions at different energy positions and with different weights. The energy region around E_1 comes from electronic states of high symmetry in reciprocal space, and what the results of Fig. 5 are telling us is that the physical interaction of Sb with either Ga or As, right at the surface, change this symmetry quite differently. Thus, the Sb perturbs the electronic states of the structure, that include the surface, subsurface and bulk regions, in such a way, that the optical signal changes, and needless to say, this change is different along the two perpendicular surface directions shown in Fig. 2. What is really impressive, is that for small or large Sb-coverage, the RAS signal differs significantly from the clean or 1 ML surfaces, respectively, demonstrating how the RAS is quite sensitive to small deviations of a given surface, i.e. one needs just small number of extra Sb or missing Sb atoms, to get a different optical response. The same argument could be applied to some other energy for which there are differences in the RAS signal for the two bonding sites.

We mention that the differences in the total energy obtained through the relaxation process for the Ga-bonded or As-bonded partially covered Sb surfaces is rather small. Therefore, it would be difficult to assign the preferred bonding site based on energy considerations alone. However, the optical results presented above, show that RAS could be used, for this purpose, as alternative technique to those of Refs. [13, 18, 19].

4 Conclusions In summary we have studied the theoretical RAS spectra for the adsorption of Sb atoms on a clean GaAs(110) surface. We used an ab-initio method and a SETB method in order to calculate the RAS spectra. We have explored the possible preferential bonding site of Sb atoms with either Ga or As atoms. The SETB approach gives very similar RAS results for both bonding sites, mainly due to the fact that only nearest neighbor interactions are included. This may indicate that our SETB model may not represent the bonding of Sb to the clean GaAs(100) surface at the sub-monolayer level. However, for the ab-inito RAS results we have found differences in the magnitude and sign of the spectra as a function of the Sb-coverage. These features could be assigned as a signature of the possible preferential bonding site for the Sb atoms to either a Ga or a As atoms as one grows one monolayer of Sb on top of a clean GaAs(110) surface. The above results, along with the experimental spectra, could
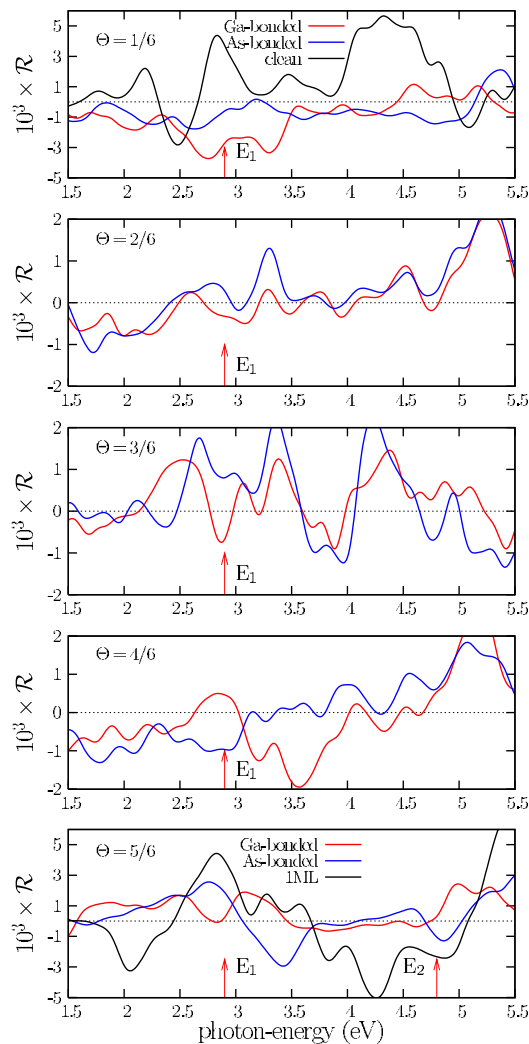

Figure 4 (Color online) SETB calculated RAS spectra for the partly Sb-covered GaAs(110) surface for coverages $\Theta = 1/6, 2/6, 3/6, 4/6, 5/6$ ML. The label Ga (As) indicates that the Sb atoms have preferential bonding to Ga (As) atoms. The corresponding RAS spectra for the clean and 1ML Sb-covered GaAs(110) surface are also shown.

be confronted with the findings of Refs. [13, 15], where it is claimed that for low Sb-coverage there is a preferential bonding site for the Sb atoms. However, to our knowledge there are no experimental RAS spectra available for the partly Sb-covered GaAs(110) surface, thus our present work is a step forward in the study of the optical response of the deposition of adsorbates on clean semiconductor surfaces. The RAS technique could give information of the preferential bonding sites for the adsorbates and the growth process on surfaces.

Figure 5 (Color online) Ab-initio calculated RAS spectra for the partly Sb-covered GaAs(110) surface for coverages $\Theta = 1/6, 2/6, 3/6, 4/6, 5/6$ ML. The label Ga (As) indicates that the Sb atoms have preferential bonding site to Ga (As) atoms. The corresponding RAS spectra for the clean and 1ML Sb-covered GaAs(110) surface are also shown.

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