Adsorbate-induced modification of the surface electronic structure at GaAs(001) surfaces

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We report on the influence of hydrocarbon ring molecule adsorption on the surface electronic properties of GaAs(001)-(2×4) and $c(4 \times 4)$ surfaces. The adsorption geometry has been published previously, and it has been shown that there are strong indications that the surface As dimer bond is cleaved upon the chemisorption of the molecules at the $c(4 \times 4)$ reconstruction whereas the As dimers remain intact at the (2×4) reconstruction. At these different interfaces we have studied the adsorption-induced modification of the surface electronic properties. The surface band bending was investigated by synchrotron-based x-ray photoelectron spectroscopy, and the surface electric field was determined optically by reflectance anisotropy spectroscopy via the linear electro-optic effect. While the band bending at the GaAs(001)-(2×4) surface remains unaffected upon molecule adsorption, the surface electronic properties of the $c(4 \times 4)$ reconstructed surface undergo substantial changes. The surface band bending is reduced by 300 meV while the surface electric field increases significantly. These observations are explained within a model for the band bending at GaAs(001) surfaces that was recently suggested by Lastras-Martínez *et al.* [Phys. Rev. Lett. **96**, 047402 (2006); Phys. Rev. B **75**, 235315 (2007)], and the results underline the important role of dimer-induced strain for the surface band structure at the GaAs(001)-$c(4 \times 4)$ surface.

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I. INTRODUCTION

The modification of the electronic properties of semiconductor surfaces owing to surface reactions plays an important role in the design of novel biosensor concepts.[1–5] Particularly, the possibility of monitoring molecular adsorption processes or intermolecular reactions via the electronic properties of a semiconductor surface opens up perspectives for a variety of new sensor developments such as laboratory-on-the-chip concepts.[6,7] For the adsorption of organic molecules on semiconductor surfaces, the surface dimer structure plays an important role for the adsorption process and the bonding configuration.[8–11] On semiconductor surfaces, on Si as well as on III-V semiconductors, the surface electronic properties depend crucially on the surface dimer structure. Only recently Lastras-Martínez *et al.* suggested that the band bending of GaAs(001) surfaces is influenced by dimer-induced strain.[12,13] A modification of the surface strain owing to molecule adsorption onto the surface dimers can, therefore, influence significantly the surface electronic properties. In this context we have investigated interfaces between (2×4) and $c(4 \times 4)$ reconstructed GaAs(001) surfaces and the unsaturated hydrocarbon ring molecules cyclopentene and 1,4-cyclohexadiene. Cyclopentene (C_5H_8) and 1,4-cyclohexadiene (C_6H_8) are unsaturated hydrocarbon ring molecules with one or two double bonds, respectively. The As-rich GaAs(001)-c (4×4) surface reconstruction exhibits a triplet of symmetric As dimers that are bonded to second layer As atoms, whereas the (2×4) reconstruction contains two symmetric As dimers in the top layer that are bonded to second-layer Ga atoms.[14,15]

In previous investigations, cyclopentene and 1,4-cyclohexadiene were shown to bond covalently via the formation of C-As bonds to the As dimers of the $c(4 \times 4)$ and (2×4) reconstructed GaAs(001) surfaces. In the case of the $c(4 \times 4)$ surface, there is evidence that the adsorption causes a splitting of the As-As dimer bond, whereas the adsorption on the (2×4) leaves the As dimer bond intact, as depicted in Fig. 1.[10,16] At the GaAs(001)-$c(4 \times 4)$ surface, the strain caused by the As dimers was recently suggested to induce a direct piezoelectric dipole (DPD) that opposes the electric field of the space-charge layer within the first monolayers.[12,13,17] A splitting of the As dimer bond, as caused by the molecule adsorption, is therefore expected to significantly modify the surface electronic properties, e. g., the band bending and the surface electric field. The investigations performed in this work are, therefore, suitable to verify the predictions made by Lastras-Martínez *et al.* in their recently suggested model concerning the role of dimer-induced strain at the GaAs(001)-$c(4 \times 4)$ surface.[12] Because the molecule adsorption does not cause a splitting of any bondings at the (2×4) reconstructed surface, the surface band bending is not expected to be modified upon molecule adsorption in this case.[16]

For the characterization of the surface electronic properties, we also investigated the surface electric field via the linear electro-optic (LEO) effect. The LEO effect on the optical anisotropy of GaAs(001) surfaces at a photon energy of ~3.0 eV was first observed by Acosta-Ortiz *et al.*,[18] and for doping levels up to 1×10^{18} cm^{-3}, the LEO effect was shown to depend linearly on the integrated surface electric field (SEF) over the reflectance anisotropy spectroscopy (RAS)sxs penetration depth.[19–22] At GaAs the penetration depth of the incident light at 3 eV amounts to ~20 nm,[19,23] which is lower than the depletion width of the samples used in this work. Recently, we have presented an enhanced background correction for LEO spectra that allows a more precise determination of the integrated surface electric field at interfaces between organic molecules and GaAs(001) surfaces.[24]

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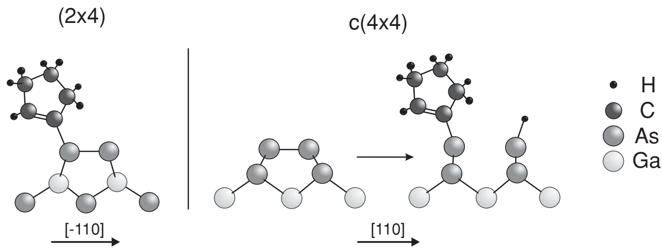

FIG. 1. Ball and stick models of the adsorption configuration of cyclopentene on the top surface dimers of the GaAs(001)-(2 × 4) surface (left-hand side) and the GaAs(001)-$c(4 \times 4)$ surface (right-hand side). At the $c(4 \times 4)$ surface, the As dimer bond breaks upon adsorption, whereas the dimer bond remains intact at the (2 × 4) surface.

II. EXPERIMENTAL

For our experiments, we used molecular-beam-epitaxy-(MBE-) grown and As-capped GaAs(001) samples with nominal Si doping of $n = 5 \times 10^{17}$ cm^{-3} unless stated otherwise. The GaAs(001) surfaces were thermally decapped, prepared, and analyzed under ultrahigh vacuum (UHV) conditions with a base pressure below 2×10^{-10} mbar throughout the experiments. GaAs(001)-$c(4 \times 4)$ and -(2 × 4) surfaces were obtained at annealing temperatures of ∼350 and 450 °C, respectively. The preparation process was monitored by RAS and the chemical and structural surface quality was checked by Auger electron spectroscopy (AES) and low-energy electron diffraction (LEED) (details are described in Ref. 10).

Cyclopentene (Aldrich, purity 97%) and 1,4-cyclohexadiene (Aldrich, purity 98%) were introduced in different experimental cycles into the chamber through a variable gas-inlet valve. During the exposure of cyclopentene or 1,4-cyclohexadiene, the GaAs(001) sample was kept at room temperature and all filaments inside the chamber were switched off in order to prevent decomposition of the molecules.

The deposition process was *in situ* monitored by a RAS setup operating in a photon energy range from 1.5 to 5.5 eV. Details on the RAS setup are described in Refs. 25 and 26. The deposition of cyclopentene and 1,4-cyclohexadiene was stopped when more changes in the RAS line shape could be seen, as described elsewhere.[10,27] This point is defined as the saturation level and was found to describe an effective molecule layer thicknesses of ∼1 monolayer (ML) in both cases.[10] The same RAS setup was used for measurements of the LEO effect at ∼3.0 eV in order to determine the integrated surface electric field.

The surface band bending was investigated by photoemission measurements at the beamlines RGBL and PM3 at the synchrotron facility BESSY II. All spectra were taken at normal emission. The total instrumental resolution (beamline plus analyzer) at an excitation energy of 75 eV was found to be 120 meV in both cases. For the analysis of the surface band bending, the valence band as well as the As 3*d* and Ga 3*d* core levels were measured. For a determination of the binding energies of the core-level spectra, the Fermi edge was determined by photoemission from a molybdenium sample holder being in ohmic contact with the samples. The core-level spectra were analyzed by numerical line-shape analysis based on nonlinear curve fitting. Details on the fitting procedure are described elsewhere.[10]

III. RESULTS

Figure 2 shows the synchrotron-based x-ray photoelectron spectroscopy (SXPS) measurements of the Ga 3*d* core level before and after cyclopentene adsorption on the (2 × 4) reconstruction (left-hand side) and the $c(4 \times 4)$ reconstruction (right-hand side). A detailed analysis of the line-shape analysis can be found in Refs. 10 and 16. The spectra taken at the (2 × 4) surface show that the energetic position of the Ga 3*d* core level does not change upon molecule adsorption. The same is observed for the As 3*d* core level and for the valence-band edge (not depicted). At the $c(4 \times 4)$ surface, however, the measurements reveal that the binding energies of the Ga 3*d* core level shift by an amount of +300 meV upon molecule adsorption. The same shift of 300 meV away from the Fermi level is observed in the As 3*d* core level and the valence-band edge (not depicted). In all cases the measurements after the adsorption of 1,4-cyclohexadiene show the same behavior (not shown here). These results indicate a significantly different influence of the molecule adsorption depending on the respective surface reconstruction and require a deeper analysis for the $c(4 \times 4)$ reconstruction.

For the further analysis of the adsorption-induced changes at the GaAs(001)-$c(4 \times 4)$ surface, the surface electric field was measured via the LEO effect with reflectance anisotropy spectroscopy. Figure 3 (left-hand side) shows the RAS spectra recorded in a photon energy range from 1.5 to 5.5 eV. As discussed elsewhere, cyclopentene and 1,4-cyclohexadiene cause essentially the same modification of the LEO feature and are therefore not distinguished here.[24] The changes at the

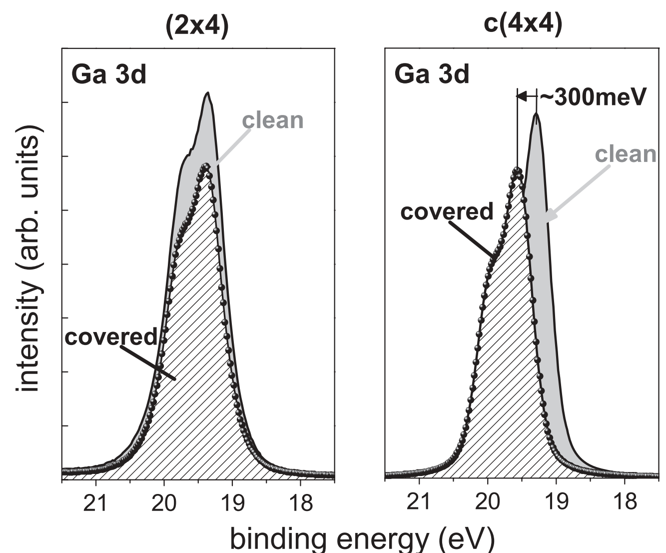

FIG. 2. Photoemission spectra of the Ga 3*d* core level before (gray) and after adsorption of cyclopentene (balls). For the (2 × 4) reconstruction (left-hand side), the energetic position of the Ga 3*d* core level is unchanged. For the $c(4 \times 4)$ reconstruction, the energetic position is shifted by ∼300 meV away from the Fermi level (right-hand side).

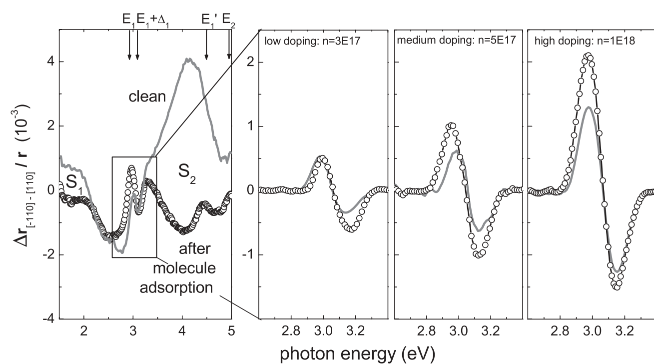

FIG. 3. Left-hand side: RAS spectra in the range from 1.5 to 5 eV. The spectrum of the clean GaAs(001)-$c(4 \times 4)$ surface is shown as a full line. The spectrum after adsorption of hydrocarbon ring molecules is illustrated with open circles. Right-hand side: LEO spectra before (full line) and after molecule adsorption (circles) in the range from 2.6 to 3.4 eV for samples with different doping levels. All spectra indicate a significant increase of the integrated surface electric field.

surface transitions labeled $S1$ below 2 eV and $S2$ at ~4 eV are associated to the breaking of the dimer bond upon molecule adsorption.[10,27] Beside these changes, a clear increase of the amplitude of the LEO oscillation in the spectral range of bulk critical points E_1, $E_1 + \Delta_1$ can be observed. In our previous work, we presented an enhanced background correction for the LEO spectra in the range from 2.6 to 3.4 eV, which allows a quantification of the surface electric field, also after molecule adsorption.[24] Figure 3 (right-hand side) shows the background-corrected LEO spectra before (full lines) and after molecule adsorption (circles) on GaAs(001)-$c(4 \times 4)$ surfaces with three different doping levels. The nominal doping level of the 1-μm-thick GaAs epilayer in the three different plots amounted to $n = 3 \times 10^{17}$ cm^{-3} (low), $n = 5 \times 10^{17}$ cm^{-3} (medium), and $n = 1 \times 10^{18}$ cm^{-3} (high). In all three cases, a significant increase of the strength of the LEO oscillation can be observed. Because the LEO effect at the GaAs(001)-$c(4 \times 4)$ surface scales linearly with the integrated surface field (ISF) for doping levels up to $n = 1 \times 10^{18}$ cm^{-3},[19,20,22,28] the spectra reveal that the integrated surface field increases upon molecule adsorption by a factor of 1.4 at low and high doped samples and 1.8 at medium doped samples, respectively.[24] For the (2×4) reconstruction, it is not possible to quantify the LEO effect from the RAS spectra after molecule adsorption in this case. Therefore, the RAS spectra cannot be used for an investigation of the surface electric field after molecule adsorption. Because, however, no changes were observed at the surface band bending, there is no reason to expect a modification of the surface electric field in this case.

IV. DISCUSSION

Summarizing the measurements at the $c(4 \times 4)$ surface, two effects can be observed after molecule adsorption: (1) a decrease of the surface band bending of 300 meV and (2) an increase of the magnitude of the integrated surface field. Within the conventional model of the surface band bending, these two observations are contradictive. Assuming a linearly decreasing electric field with a gradient determined by the doping level, an increase of the magnitude of the integrated surface field should correlate to a higher band bending and can therefore not be explained within this model. However, Lastras-Martínez *et al.* recently suggested that for GaAs(001) the surface band structure is significantly influenced by a piezoelectric dipole induced by the strain of the As dimers.[12,13] The effective electric field as measured by the LEO effect can be written as

$$\langle E \rangle = C \int_0^d E(z) \exp\left(\frac{-z}{d}\right) dz,$$

where d is the information depth of the RAS light. Following the model by Lastras-Martínez *et al.*, the electric field $E(z)$ over the RAS information depth at the $c(4 \times 4)$ reconstruction results from two contributions, as schematically illustrated in Fig. 4:

(1) The electric field of the space-charge layer causes an upward band bending and provides a positive contribution to the magnitude electric field measured with RAS via the linear electro-optic effect.

(2) In the topmost tens of MLs (≈10 nm), the strain produced by the topmost As dimers induces a direct piezoelectric dipole that opposes the electric field of the space-charge layer.[12,13] This DPD electric field, therefore, provides a negative contribution to the magnitude of integrated surface field measured via the LEO effect with RAS.

The strength of the LEO oscillation results from a superposition of these two opposing contributions to the integrated surface field, as schematically illustrated in Fig. 4.

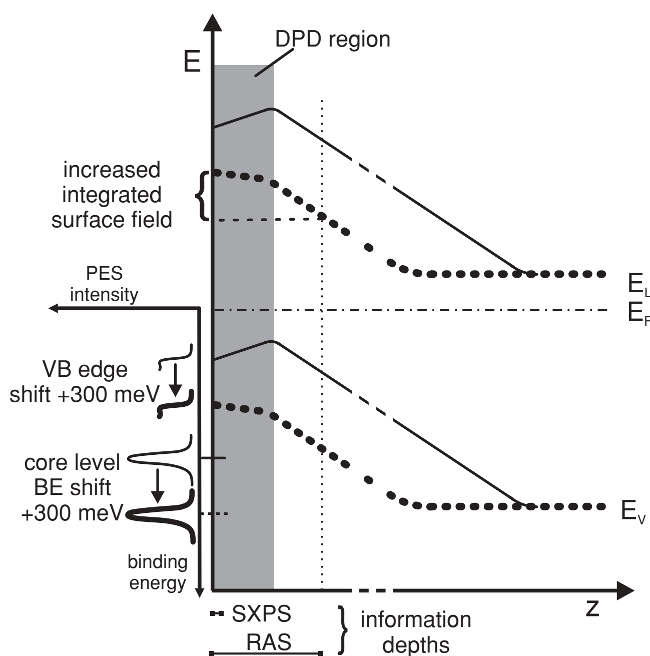

FIG. 4. Solid line: Schematic illustration of the band diagram before molecule adsorption on the $c(4 \times 4)$ surface based on Ref. 12. The strength of the LEO effect results from a superposition of the electric field of the space-charge layer and the opposing DPD electric field. Dashed line: Suggested schematic band diagram after molecule adsorption. The overall band bending decreases owing to the loss of surface states, while in the surface region the opposing DPD contribution is reduced owing to the reduction of dimer-induced strain.

Based on this model we can explain the observations described above in the following way. Several possible influences on the different contributions to the electric field have to be considered in detail: (1) a new contribution to the integrated surface field from an electric dipole within the adsorbed molecular film, (2) a modification of the electric field of the space-charge layer, and (3) a modification of the strain-induced piezoelectric dipole (DPD).

If the observed increase of the integrated surface field originated from a new contribution to the electric field, e. g., an electric dipole of the adsorbed molecular layer, it would have to be of the same magnitude irrespective of the substrate doping level. Our measurements, however, show that the observed increase is not the same at all investigated samples but varies with the substrate doping level. Also, we observe the same behavior of the band bending for two different molecules (cyclopentene and 1,4-cyclohexadiene). Thus, our observations cannot be explained sufficiently by a new contribution to the electric field from the molecular layer but need to originate from a modification of the electronic properties of the substrate. This could be either the modification of the electric field of the space-charge layer or the modification of the strain-induced DPD.

The positive contribution to the magnitude of the integrated surface field from the space-charge layer is a material characteristic depending on the doping level of the GaAs substrate and the amount of surface states. Our RAS measurements show that the number of surface states decreases upon molecule adsorption. This observed decrease of the number of surface states can, however, only result in a decrease of the magnitude of the integrated surface field. Therefore, it cannot be responsible for the observed increase of the LEO effect.

The only possible explanation left is to be found in an adsorption-induced modification of the surface strain. According to Lastras-Martínez *et al.*, the DPD electric dipole is caused by the strain produced by the As dimers of the GaAs(001)-$c(4 \times 4)$ surface, and contributes negatively to the magnitude of the integrated surface field because it opposes the electric field of the space-charge layer. Our observations can be explained only by this model if the dimer-induced surface strain is reduced upon adsorption of cyclopentene and 1,4-cyclohexadiene. The only way of achieving this is by changing the surface dimer structure, i.e., by cleavage of the top As-As dimers. Consequently, the results presented here give further evidence for our earlier conclusion that the As dimers are cleaved upon adsorption of hydrocarbon ring molecules.[10]

Taking into account the considerations described above, the electronic properties of the GaAs(001)-$c(4 \times 4)$ surface undergo substantial changes upon the adsorption-induced cleavage of the As-As dimers. First, the adsorption process reduces the amount of surface states as observed by RAS, which reduces the overall band bending significantly. This results in a shift of the core-level binding energies in the surface region as measured by SXPS (see Fig. 2). Second, at the same time, the cleavage of the As-As dimers at the surface reduces the strain-induced DPD that opposes the electric field of the space-charge region. Because this DPD contributes negatively to the magnitude of the integrated surface field, the DPD reduction leads to an increase of the magnitude of the integrated surface field as observed via the LEO effect.

The dashed curve in Fig. 4 illustrates schematically how the superposition of these different effects can be visualized within the band diagram suggested by Lastras-Martínez *et al.*[12] Please note the different information depths of SXPS ($\leqslant$1 nm) and RAS ($\geqslant$15 nm) as compared to the DPD penetration depth ($\approx$10 nm).

These results support the model suggested by Lastras-Martínez *et al.*[12] and open up new perspectives for systematic investigations of adsorption-induced dimer cleavage at GaAs(001) surfaces. Our results show that the modification of surface strain owing to molecule adsorption can have a significant influence on the electronic properties of the interface. For adsorption experiments of molecules on GaAs(001) surfaces, it will therefore be important to clarify whether or not the surface strain is affected, e.g., by cleavage of the top surface dimers during the respective adsorption process.

V. SUMMARY

We have been able to demonstrate that the adsorption-induced cleavage of the surface dimer bonds causes a significant modification of the surface electronic structure of GaAs(001) surfaces. At the GaAs(001) (2×4) surface, the surface band bending remains unchanged because all surface bonds, particularly the bonds of the As dimers, remain intact. At the GaAs(001)-$c(4 \times 4)$ surface, the molecule adsorption causes an increase of the magnitude of the integrated surface field and a reduction of the surface band bending by 300 meV. Based on the model for the surface band bending at the GaAs(001) surface suggested by Lastras-Martínez *et al.*,[12,13] these observations can only be explained by a reduction of the strain-induced DPD electric field on account of the splitting of the As-As dimer bond during the chemisorption process.

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