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Ge/GaAs(001) interface formation investigated by reflectance anisotropy spectroscopy

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The formation of the Ge/GaAs(001) interface has been investigated following the transformation of an As-dimer terminated GaAs(001)(2×4) surface into a Ge-Ga-dimer terminated (1×2) reconstruction and the subsequent deposition up to 10 ML of Ge. The modification of the surface atomic geometry and the related electronic structure has been monitored by reflectance anisotropy spectroscopy (RAS) and low-energy electron diffraction. Experimental results are compared to density-functional-theory–local-density-approximation and tight-binding calculations of the surface structure and optical response, respectively. The comparison between calculated and measured RAS spectra allows us to show that the (2×4) structure transforms into a well-ordered (1×2) passing through a disordered (2×4) phase while a previously proposed intermediate (2×1) structure is ruled out. At higher Ge coverages, surface and Ge/GaAs-interface contributions to the optical spectra are separated by surface modification through exposure to atmosphere. A interface contribution is identified between 1.5 eV and 2.5 eV, almost identical in line shape and amplitude to the RAS features on the Ge-Ga-dimer terminated GaAs surface. This finding demonstrates that the backbonds of the Ge-Ga-dimers, present at the Ge-Ga-dimer terminated surface as well as at the Ge/GaAs interface, determine the optical anisotropy, whereas the Ge-Ga-dimer bond itself does not contribute significantly. [S0163-1829(99)12315-4]

I. INTRODUCTION

In recent years, reflectance anisotropy spectroscopy (RAS) has been increasingly used as an *in situ* optical technique for monitoring the atomic surface structures, the passivation of surfaces and the growth of epitaxial layers in metal-organic vapor-phase epitaxy (MOVPE) and molecular-Beam epitaxy (MBE).[1–6]

The theoretical understanding of the spectra is also fast developing.[4,7–11] For various reconstructions of the As-terminated GaAs(001) surfaces, for example, we have shown recently[9,11] that the RAS spectra can be modeled rather accurately on the basis of band-structure calculations, if realistic atomic surface structures are available. In turn, the comparison of RAS spectra with calculations for different structural models thus can be used as a sensitive test to discriminate the real structure among competitive models. The motivation of our present study is to determine the atomic structure of the Ge/GaAs(001) interface by comparing the measured and calculated RAS spectra, the latter being obtained with the same theoretical approach as in Ref. 11.

The early stage of the Ge/GaAs(001) interface formation has been studied by different surface-sensitive spectroscopies: photoemission,[12–14] scanning tunneling microscopy (STM),[15,16] and medium energy ion scattering (MEIS).[17] It was found that 0.5 ML Ge on GaAs(001) (2×4) forms a well-ordered and stable (1×2) structure after annealing at 875 K, passing through a rather disordered (2×1)-like phase around 700 K. For higher coverages, the formation of Ge islands was reported, exposing the (1×2) reconstructed surface in between the islands.[16] In order to explain the evolution of the low-energy electron diffraction (LEED) and STM patterns at 0.5 ML of Ge coverage, the subsequent formation of Ge-As-dimers {along the $[1\bar{1}0]$ direction, (2×1) reconstruction} at lower and Ge-Ga-dimers {along the $[110]$ direction, (1×2) reconstruction} at higher temperatures, respectively, was suggested. More recently, on the basis of *ab initio* total-energy minimization,[18] buckled Ge-As and Ge-Ga dimers were proposed to build up the (2×1) and (1×2) reconstructions. However, no direct experimental confirmation of the Ge-As and Ge-Ga dimers has been reported.

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In this work we use RAS and LEED to monitor the modification of the atomic and electronic structure of the GaAs(001) (2×4) surface following the experimental sequence as described in the STM studies.[15,16] Comparing calculated and measured RAS spectra, we are able to show that the (2×4) phase transforms into the well-ordered (1×2) phase passing through a disordered (2×4) structure. The formerly proposed (2×1) phase[15] does not exist.

At higher Ge coverages we separate surface and interface contributions to the RAS spectra through exposure to atmosphere. We find that the main RAS features are related to the backbonds of the Ge-Ga dimers—i.e., to the bonds between the Ge-Ga dimers and the As atoms in the underlying layer—and to modifications of the bulk electronic structure.

II. EXPERIMENT

The GaAs samples consisted of epitaxial GaAs buffer layers, grown by MBE on GaAs(001) substrate and capped with an amorphous As layer. Two Si-doping concentrations were used in this study: $n=1\times10^{18}$ and $n=1\times10^{16}\ \mathrm{cm}^{-3}$. In the following we use HD and LD to label the high and low doped samples, respectively.

After transfer through air, the samples were investigated in an UHV chamber equipped with a cylindrical mirror analyzer type Auger electron spectroscopy (AES) unit and a four grid reverse view LEED optic. The RAS setup was placed in front of a strain-free quartz window of the UHV chamber. Clean GaAs(001) (2×4) surfaces were prepared by thermal desorption of the As cap layer and annealing at approximately 670 K. The heating was performed by a hot filament from the backside of the sample while the temperature was monitored by a calibrated thermocouple attached to the sample manipulator. The decapping procedure was monitored by the sample temperature, the pressure in the chamber, and by quadrupole mass spectroscopy (QMS). For the Ge evaporation a MBE cell was used. During 0.5 ML and 10 ML Ge evaporations the substrate was kept at 600 K and 700 K, respectively, and the pressure in the chamber was kept below 2×10^{-8} mbar, while the background pressure in the chamber was $\leqslant10^{-10}$ mbar. The Ge evaporator was calibrated by AES recorded after deposition of few Ge layers (up to 10 ML). In RAS the results are commonly reported in terms of $\Delta\tilde{r}/\tilde{r}=\Delta r/r+i\Delta\theta$, where $\tilde{r}=r\exp(i\theta)$ is the complex reflectance, and $\Delta\tilde{r}$ is defined as $\Delta\tilde{r}=\tilde{r}_{1\bar{1}0}-\tilde{r}_{110}$ (the subscript denotes the polarization vector). In the following we show only the real part of $\Delta r/r$. All spectra were recorded after cooling the sample to room temperature (RT).

III. THEORETICAL DETAILS

The surface geometry for the Ge-covered GaAs(001) surface was determined by total-energy (TE) minimization using density-functional theory within the local-density approximation (DFT-LDA). We considered a (001) periodic slab of eight atomic layers plus a vacuum region equivalent in thickness. The last two layers of the slab were fixed in a bulklike ideal position, while the back side of the slab has been saturated by fictious, fractionally charged H atoms. Single particle orbitals were expanded into plane waves up to an energy cutoff of 12 Ry. Four special k points have been used in the irreducible part of the two-dimensional surface Brillouin zone (2DBZ). Atomic coordinates have been relaxed using the Car-Parrinello molecular dynamics scheme[19] using a $p(2\times2)$ supercell. Three different structures were considered in the calculations, i.e., the Ge-As-dimer terminated (2×1)-, the Ge-Ga-dimer terminated (1×2)- and a Ge-As-dimer terminated $\beta2\ (2\times4)$-like structure, the latter formed by random substitution of one of the As atoms in the As dimers by Ge. In the latter structure a number of different configurations, depending on the relative positions of the Ge atoms in the dimers, were considered. The atomic structure data of GaAs(001) $\beta2\ (2\times4)$ were taken from Schmidt and Bechstedt.[20]

For the (2×1) phase the Ge-As-dimer bond length was found to be 2.37 Å. The As is raised up with respect to Ge in the dimer producing a buckling of 0.69 Å. The Ge-Ga-dimer length for the (1×2) phase is 2.48 Å, with Ge raised up with respect to Ga by 0.76 Å. We would expect buckled dimers due to the chemical nonequivalence of Ge with respect to the more electronegative As and less electronegative Ga. Nevertheless there is still no experimental evidence for a dimer buckling. The above values for (2×1) and (1×2) structures are similar to those reported by Srivastava and Jenkins.[18] Our results, however, are obtained with more than twice the number of plane waves, a thicker slab and larger (2×2) supercell. Using a thicker slab allows us to follow carefully the subsurface lattice relaxation, which is important for the optical properties.

After having determined the atomic surface structure by TE minimization the reflectance anisotropy was calculated within the sp^3s* tight-binding approach.[4,7,11] To separate the contributions of the two nonequivalent opposite surfaces of the slab, we applied a linear cutoff function when calculating the optical matrix elements. A slab of 20 atomic layers has been chosen to avoid the spurious interaction between the opposite surfaces of the slab. 64 special k points have been used within the $p(2\times2)$ supercell, equivalent to the 256 k points in the irreducible part of the 2DBZ of the (1×1) unit cell. Other technical details for the calculation of the surface optical response [including that one for mixed Ge-As dimers for the $\beta2\ (2\times4)$-like phase] are similar to that of Ref. 11.

IV. RESULTS AND DISCUSSION

In Figs. 1(a) and 1(b) the RAS spectra of the clean surfaces and their evolution after Ge deposition and subsequent annealing is shown for a HD and a LD sample, the corresponding LEED patterns are also indicated in the figures. The RAS spectra for the clean surfaces (curves a) show the typical, well-known line shape of a (2×4)-reconstructed surface.[1–4,6] The linear electro-optical (LEO) oscillation[21,22] related to the surface electric field induced by the band bending is superimposed at 2.9 eV and 3.1 eV, the E_1-, $E_1+\Delta_1$-gaps of GaAs. The difference in amplitude of the LEO oscillation in Figs. 1(a) and 1(b) reflects the doping concentrations of the two samples (high electric field in the HD sample, low electric field in the LD one).

The corresponding LEED patterns show (2×4) structures in both cases. After 0.5 ML Ge deposition, a drastic reduction in the intensity of the peak at 2.8 eV together with the development of a negative contribution at lower energies is

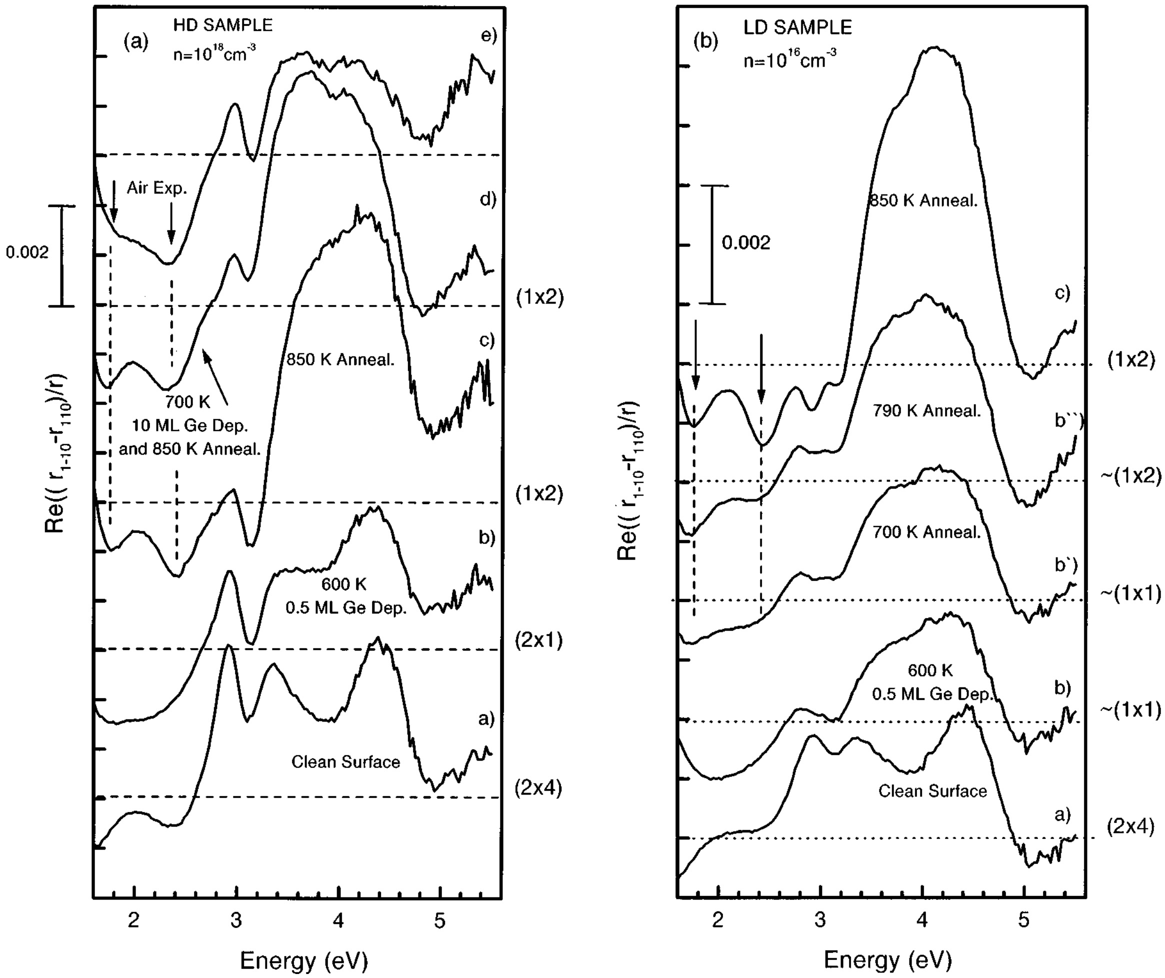

FIG. 1. The real part of the room temperature RAS spectra of high (a) and low (b) *n*-doped GaAs (100). (a) (2×4) clean surface; (b) after 0.5 ML of Ge deposition at 600 K; (c) after subsequent annealing at 850 K; (d) after deposition of 10 ML Ge at 700 K and subsequent annealing at 850 K; (e) after air exposure. The corresponding LEED patterns are also indicated. The dashed horizontal lines denote the zero levels for each spectrum. The arrows mark features related to surface/interface contributions.

visible (curves *b*). The high-energy part of the spectrum remains almost the same. On the LD sample, an additional broad structure at approximately 3.6 eV occurs. The LEED pattern shows a weak (2×1) pattern for the HD sample and a (1×1) pattern for the LD one.

After annealing to 850 K for 5 min the LEED pattern changes in both cases to a sharp (1×2). At this stage, As atoms of the top atomic layer are desorbed and Ge-Ga-dimers are expected to terminate the surface, giving rise to the (1×2) ordering.[15] In the corresponding RAS spectra, curves *c*, the negative feature is now well pronounced, and two structures at 1.8 eV and 2.4 eV are clearly visible. At higher energies a strong, broad peak develops for both the HD and the LD sample. The LEO oscillation decreases on the HD sample upon going from the clean (2×4) ordered surface to the (1×2) one. On the LD sample, the initial LEO oscillation vanishes after 0.5 ML Ge deposition and appears again with the opposite sign after annealing at 830 K. We attribute these effects to the diffusion of Ge into the bulk thereby changing the doping concentration and, correspondingly, the accompanied electric field in the near-surface region.[23]

Annealing cycles at intermediate temperatures were performed on the LD sample. The RAS spectra (curves *b*′ and *b*″) show how the two negative peaks start to develop after annealing at 700 K and become more pronounced with increasing annealing temperature. The corresponding LEED pattern is (1×1) until finally, after the annealing at 790 K, a twofold periodicity develops along the [110] direction.

We want to underline here that the development of the RAS spectra is not consistent with the existence of two distinct [i.e., Ge-As-(2×1) and Ge-Ga-(1×2)] structures, since all significant RAS features of the Ge-Ga-(1×2) surface are present already after Ge deposition. With increasing degree of surface ordering during subsequent annealing the negative feature at approximately 2 eV sharpens only, developing into two minima. Any distinct RAS features as expected for indicating the (2×1) phase are completely missing. Thus the evolution of the RAS spectra would rather suggest the destruction of the initial (2×4) surface structure upon Ge deposition followed by the formation of a (1×2) structure with subsequent annealing.

After the deposition of 10 ML of Ge at 700 K on the HD sample and subsequent annealing for 5 min at 850 K, the surface still shows a good (1×2) LEED pattern. The corresponding RAS spectrum [Fig. 1(a), curve *d*] is characterized

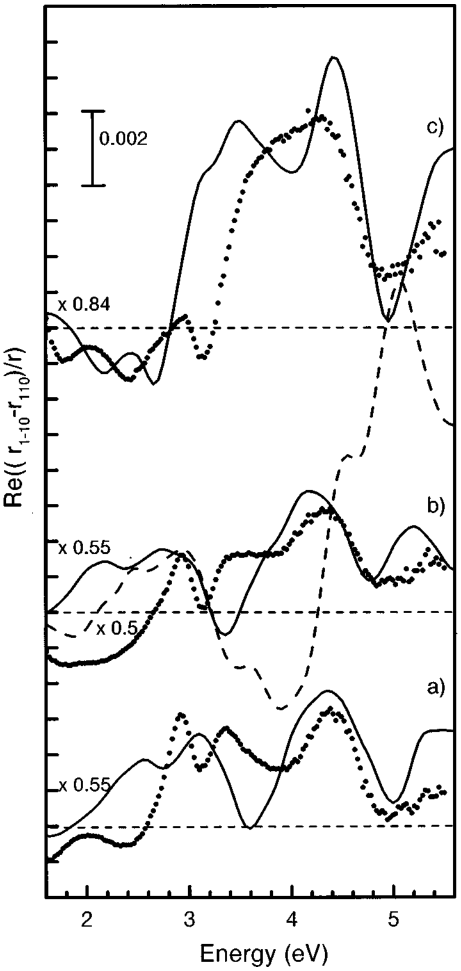

FIG. 2. Comparison between the RAS spectra of Fig. 1(a) and the calculated spectra for (a) the $\beta2$ (2×4) phase of the clean surface; (b) the (2×1) phase (dashed line) and the β $2(2\times4)$-like phase with Ge-As dimers (solid line); (c) the (1×2) phase.

by an increase in amplitude of the peak at $\simeq 3.7$ eV. No significant changes are observed in the low-energy part. Ge islands are expected to be formed at high coverage while the (1×2) order persists on the surface in between the islands.[16]

The sample was then exposed to air for a few days, and measured again by RAS. The spectrum is shown in Fig. 1(a), curve e. The negative structures at 1.8 eV and 2.4 eV are broadened but still clearly present. The structures at 3.7 eV and 4 eV are also still present, but with a smaller amplitude. This is an indication that all these features are related to Ge induced bulk modifiations and to Ge-Ga dimer backbonds, present at the Ge-Ga-dimer terminated surface as well as at the Ge/GaAs interface. They are not affected by the oxidation as the interface is protected by the Ge islands.

V. COMPARISON TO CALCULATIONS

In Fig. 2 the calculated and experimental RAS spectra are compared. The theoretical curve for the $\beta2$ (2×4) structure[9] is plotted in Fig. 2(a) together with the corresponding experimental curve of the clean GaAs(001) adapted from Fig. 1(a). The positions of the main peaks and the line shape of the calculated RAS curve correspond quite well to the experimental one (for further details see Refs. 9 and 11; the LEO effect is not included in the calculation).

In Fig. 2(b) the calculated RAS spectrum for a ordered (2×1) As-Ge-dimer terminated structure (dashed line), the Ge-substituted (2×4) structure (solid line), and the experimental curve (b) of Fig. 1(a) (dots) are compared. One can immediately admit a strong disagreement between the calculated RAS spectrum for the ordered (2×1)-structure and the experimental RAS for the (2×1)-like phase. An essentially better agreement is found to the $\beta2$ (2×4)-like structure with the mixed Ge-As dimers. A significant deviation occurs only in the low-energy region where the experimental data show a broad, negative feature. We would like to note that the Ge substituted (2×4) model structure used in the calculations is only a crude approximation to the real structure since disorder effects cannot accurately be taken into account.

Both the calculation and the evolution of the RAS spectra during the initial stages of the Ge/GaAs(001) interface formation thus suggests that the previously proposed formation of As-Ge dimers does not describe the (2×1) phase. Instead we relate the (2×1) LEED pattern to a disordered (2×4) phase, in which Ge atoms randomly substitute one of the As atoms in the surface dimers.

In Fig. 2(c), the theoretical and the experimental RAS curves related to the (1×2) phase are compared. Two negative features are present in the calculated spectrum at 2.15 eV and 2.65 eV, and a positive feature with two peaks at 3.5 eV and 4.4 eV. The two negative peaks are also observed experimentally but shifted in energy by $\simeq 0.35$ eV. Such energy shifts between calculations and experimental data of optical spectra are a well known, common problem of band-structure calculations.[24] The two large positive features are also experimentally observed but with a broader line shape. The rather good agreement between the RAS data and calculations indicates that, contrary to the case of the (2×1) phase discussed above, the (1×2) ordered mixed Ge-Ga-dimer structure is indeed formed as proposed in Ref. 15.

The similarity in the high-energy part of the spectra of the clean GaAs(001) $\beta2$ (2×4) structure and of the Ge-As-dimer terminated (2×4) phase indicates that this part mainly originates from the structure-independent effect of the bulk termination on the wave functions. Below 3.5 eV the RAS spectra for both clean and Ge-modified GaAs(001) surfaces are, in contrast, mainly surface structure dependent. In particular, on the basis of our calculations the negative features at low energies can be attributed to electronic states localized at the backbonds of the Ge-Ga dimers. This result corroborates well with the experimental finding that these features also exist at the Ge/GaAs interface. A similar negative feature is also observed on the disordered Ge-As-terminated (2×1) surface [Fig. 2(b)] indicating that already the disruption of the As-terminated (2×4) surface includes a partial Ga substitition of the second atomic layer by Ge. This contribution is not accounted for in the Ge-substituted (2×4) model structure used for the calculations.

VI. CONCLUSIONS

In conclusion, the initial stages of the Ge/GaAs(001) formation have been investigated combining LEED, RAS, and theoretical modeling of the atomic structure and their optical properties. We have found that the atomic structure of the intermediate phase between the clean surface and the ordered (1×2) phase is given by a disordered (2×4)-like structure formed by partial substitution of As and Ga in the first and second atomic layers, respectively.

The (1×2) structure reached after annealing above 830 K corresponds to a well-ordered Ge-Ga-dimer structure, as previously suggested. According to our microscopic calculation of the surface optical anisotropy and to the observed evolution of the RAS spectra after exposure to air, the low-energy features in the RAS spectra characteristic for the Ge-Ga-dimer structure are mainly correlated to the backbonds of the Ge-Ga dimers.

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[23] This effect will be discussed in detail in a successive paper.

[24] Due to a well-known problem of a description of the excited states in semiconductors such a shift (usually called ‘‘scissor operator approximation’’) depends on the energy. That is, the shift of the excited states is not rigid.