Atomic Structure of the Sb-Stabilized GaAs(100)-(2 × 4) Surface

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The microscopic structure of the Sb stabilized GaAs(100)-(2 × 4) surfaces is investigated combining reflectance anisotropy spectroscopy with first-principles total energy minimization and tight-binding calculations of optical properties. We show that the model accepted so far, containing three Sb dimers in the outermost layer, is not a stable surface geometry. Our results reveal a coexistence of Sb and Ga dimers on the Sb-stabilized (2 × 4) surface. [S0031-9007(96)01679-1]

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Understanding of the surface atomic structures and their modification through deposition of foreign atoms is crucial for both science and technology. In particular, the adsorption of group-V elements on (100) faces of III-V compound semiconductors is technologically important for the III-V heteroepitaxy [1]. Especially the adsorption of Sb on GaAs(100) has attracted interest due to the formation of an exceptionally abrupt interface [1,2] and the possible use of Sb as surfactant for metal growth on GaAs(100) [3,4]. Soft x-ray photoemission spectroscopy (SXPS), Auger electron spectroscopy (AES), and electron diffraction [LEED and reflection high-energy electron diffraction (RHEED), respectively] studies have shown that by Sb deposition on GaAs(100) and subsequent annealing a well-ordered (2 × 4) reconstruction is formed even at temperatures much higher than for the clean, As-terminated surface, due to stabilization by Sb dimers [1,5,6].

Based on SXPS data and on the (2 × 4) RHEED pattern a first structural model for the Sb-induced reconstruction was suggested [1]. This model, based on three Sb dimers per surface unit cell, was constructed in analogy to the so-called GaAs(100)$\beta(2 \times 4)$ structure, widely used in the past to describe As-terminated GaAs(100)-(2 × 4) surfaces [7,8]. For the clean GaAs(100)-(2 × 4) surface, however, recent experimental and theoretical studies have demonstrated that the equilibrium structure contains only two As dimers per unit cell in the topmost atomic layer, denoted as $\beta 2(2 \times 4)$ structure [9–12]. As shown in Ref. [9], the electrostatic interaction between the negatively charged surface As dimers destabilizes the three-dimer compared to the two-dimer structure. The same argument should hold if the As dimers are substituted by another group-V element like Sb, thus questioning the validity of the suggested structure for the Sb-stabilized (2 × 4) GaAs(100) surface. Meanwhile, x-ray standing wave (XSW) experiments [13] confirmed the existence of Sb dimers on the surface; however, conclusive results about the validity of the three-Sb-dimer model [1] were not obtained.

The present study is aimed at the determination of the atomic structure of the Sb-stabilized GaAs(100)-(2 × 4) surface, using a novel approach to investigate microscopic surface properties based on the surface optical response. We apply reflectance anisotropy spectroscopy (RAS), *ab initio* total-energy minimization (TE), and tight-binding (TB) calculations of optical properties to study the precise surface geometry. Formation energies and geometrical data are derived from TE minimization. In order to distinguish between energetically stable structures, RAS spectra are recorded and compared with corresponding TB calculations on the basis of the TE-derived surface geometries. The experimental as well as theoretical results show that the surface optical anisotropy depends sensitively on the structural arrangement of the surface atoms. Therefore we conclude that for the successful calculation of RAS spectra the accurate determination of the atomic geometry is of crucial importance. We emphasize that also for clean GaAs(100) surfaces the optical response which we calculate by TB using TE-optimized surface structures is in much better agreement with the experimental data than what was reported in previous attempts [14,15]. Contributions not described by the TB approach such as many body effects [16] consequently should play a minor role.

For the analysis of the Sb-stabilized surface we consider a few plausible surface geometries which fit the (2 × 4) symmetry and contain Sb dimers on the surface. Furthermore, taking into account the chemical similarity of As and Sb, similar structural elements (Sb, As, and Ga dimers) are expected on clean and Sb-stabilized GaAs(100) surfaces. Three structures which are rather close in formation energy, $\alpha(2 \times 4)$, $\beta(2 \times 4)$, and $\beta2(2 \times 4)$, have been discussed for the clean GaAs(100) surface [9]. Therefore, it is reasonable to consider structures which are derived from those. Apart from the three-Sb-dimer structure related to the $\beta(2 \times 4)$ structure by replacement of top-layer As by Sb (model I in Fig. 1), three other structures denoted as models II–IV (Fig. 1) with two top-layer Sb dimers are derived in such a way, all being consistent with electron counting heuristics [17]. Model II is derived from the $\alpha(2 \times 4)$ and models III and IV from the $\beta2(2 \times 4)$ structure.

To determine the relaxed geometries of the four models shown in Fig. 1 we apply the density-functional theory in local-density approximation. We consider a periodic slab of eight atomic (100) layers within a (2×4) supercell and a vacuum region equivalent in thickness. The Ga-terminated surface of the slab is saturated with fractionally ($Z = 1.25$) charged H atoms. Single-particle orbitals are expanded into plane waves up to an energy cutoff of 15 Ry. We use four special **k**-points in the irreducible part of the two-dimensional surface Brillouin zone (2DBZ). This approach (cf. Ref. [18]) has proven successful in determining precisely the structural and dynamical properties of the Sb/GaAs(110) interface [19]. The ground state geometries for the adsorption models were derived by relaxing a series of structures with buckled and twisted dimers until the forces acting on the atoms were below 0.025 eV/Å. The minimum energy configurations are characterized by nearly symmetric surface dimers and a nearly planar bonding of the threefold coordinated second-layer Ga atoms. The calculated Sb-dimer length of 2.86–2.87 Å for all structures is rather close to the value of 2.95 ± 0.06 Å determined by XSW [13]. The length of the Ga dimers of model II is 2.46 Å.

Because of the different numbers of Sb and Ga atoms per surface unit cell the comparison of the TE for different models has to take into account the Sb and Ga chemical potentials. Upper limits on the chemical potentials μ are set by the bulk elements [20]. In order to give an estimate of the stability of the different surface structures we show in Fig. 2 the phase diagram obtained as a function of th Sb and Ga chemical potentials. We find that in the extreme limit, where the Sb and Ga chemical potentials equal those of the respective bulk phases, model IV is the most stable adsorption configuration. Models II and III are more favorable for lower values of μ(Sb) and μ(Ga). Model I is unstable independent of the assumed chemical potentials: its total energy is 0.037 eV per (1×1) surface unit cell higher than for model IV. This energetical difference roughly equals the one found between the β and $\beta2$ reconstruction of the clean GaAs(100)-(2×4) surface [9,10].

Because of the sensitivity of the formation energy of the three remaining models on the chemical environment, no precise prediction of the surface structure is possible solely on grounds of the energetical arguments. Therefore, the genesis of the surface structure was investigated by RAS, LEED, and AES. 2 ML of Sb were deposited onto clean, (2×4) reconstructed GaAs(100) surfaces prepared by As decapping [21] and subsequently annealed up to 500 °C. This preparation is analogous to the procedure used in the previous SXPS and XSW experiments leading reproducibly to the formation of an Sb-stabilized (2×4) reconstruction by desorption of excess Sb [1,6,22]. The optical anisotropy and the according LEED periodicity are shown in Fig. 3 for various preparation stages. The RAS spectrum of the As-terminated GaAs(100)-(2×4) surface (curve *a*) shows the well-known line shape characterized by two main positive peaks at 2.9 and 4.4 eV. In previous investigations the origin of this optical anisotropy was suggested to be related to the existence of surface As dimers [23]. This explanation is consistent with the further development of the anisotropy shown in Fig. 3: Deposition of 1 ML Sb (curve *b*) causes a strong reduction

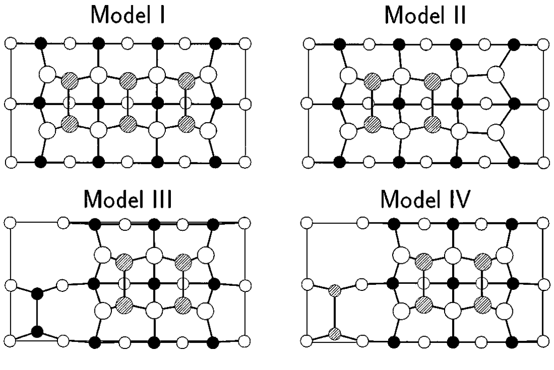

FIG. 1. Top view of relaxed Sb/GaAs(100)-(2×4) structures. Large (small) circles indicate top and second (third and fourth) layer atoms. Substrate anions (substrate cations, antimony atoms) are denoted by full (empty, shaded) symbols.

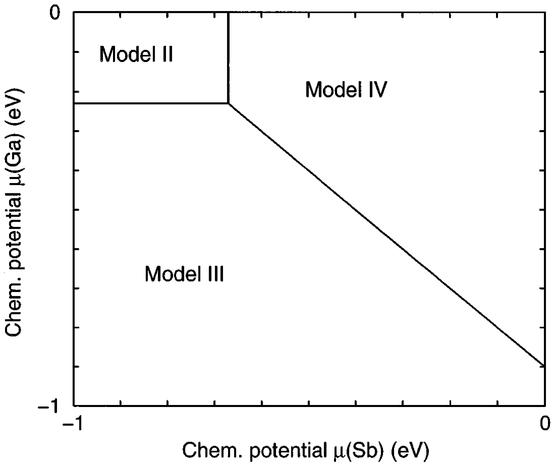

FIG. 2. Phase diagram of the Sb-stabilized structures (cf. Fig. 1) versus the Sb and Ga chemical potentials in the respective range of $-1\ \text{eV} \leq \mu - \mu_{\text{bulk}} \leq 0$. Model I is no equilibrium structure, independent of the Sb and Ga chemical potentials.

of the optical anisotropy over the entire spectral range which can be understood as the consequence of breaking the surface As dimer bonds upon Sb adsorption. A broad positive anisotropy around 4–4.5 eV develops after deposition of additional Sb (curve *c*) related to the optical properties of the thin Sb overlayer [24]. New anisotropy features arise with the ordering process induced by annealing: For the intermediate annealing step, a negative anisotropy around 2 eV and a positive feature around 4.2 eV develop (*d*). At this stage LEED shows a pattern of (3×8)-like symmetry. After annealing to 500 °C the Sb-stabilized (2×4) reconstruction is established (*e*), showing pronounced anisotropies at 2.2 eV (negative) and at 3.0 and 4.5 eV (positive).

The main spectral features of the RAS spectrum of the Sb-stabilized (2×4) surface are also found on clean, As- or Ga-terminated GaAs(100) surfaces: the dominating feature of Ga dimer terminated surfaces is a strong negative dip at 2.2 eV [23], while the As dimer terminated one shows positive features at higher energies [Fig. 3(a)]. The RAS spectrum of the Sb-stabilized (2×4) surface [Fig. 3(e)] thus resembles a superposition of both, which might indicate the coexistence of Ga dimers with As or Sb dimers on the surface. Since SXPS and XSW results showed the complete removal of the surface As dimers by replacement through Sb [1,3], Ga and Sb dimers should coexist at the surface.

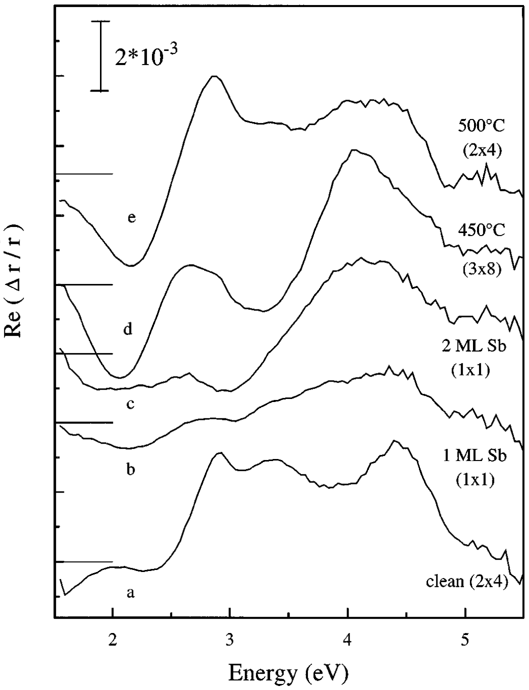

FIG. 3. Modification of the real part of $\frac{\Delta r}{\bar{r}} = \frac{r[1\bar{1}0]-r[110]}{\bar{r}}$ for GaAs(100) (n doped 1×10^{16} cm^{-3}) during Sb deposition and annealing. The spectra are taken after cooling to room temperature. The zero value for each spectrum is marked by a long tick mark.

This interpretation is substantiated by our TB calculations of the optical anisotropy for the structures shown in Fig. 1. A semiempirical tight-binding approach on sp^3s^* orbital basis [25] was used. To avoid the spurious optical anisotropy effects due to the BZ summation, we use a $p(4 \times 4)$ supercell and four special **k**-points of the irreducible part of the 2DBZ for a 20 layers slab, thus producing well converged optical properties. This approach has been intensively and successfully tested, describing the optical anisotropy of the clean and Sb-covered (110) III-V compound surfaces. The studies of clean and Sb-covered GaAs, GaP, InAs, and InP(110) surfaces have demonstrated that chemically and *geometrically* similar structures produce very similar RAS spectra [26,27].

The same relation is found for the (100) surfaces: the optical anisotropy calculated for models I to IV turns out to be very similar to that calculated for the corresponding As-terminated surface structures. Figure 4 shows the calculated RAS curves for the competitive models II, III, and IV of the Sb-stabilized surface. All three structures show a positive anisotropy at higher energies. For model IV, positive anisotropies arise above 3.5 eV, for model III around 3 and 4 eV. For model II, containing second-layer Ga dimers, in addition to the positive features at 3 eV and above 4 eV, a negative structure around 1.8 eV is found. This negative feature in the calculated optical anisotropy (obtained for both Sb-stabilized and clean, Ga-terminated surfaces) is connected to the presence of surface Ga dimers, corresponding to the negative anisotropy observed experimentally at 2.2 eV for clean, Ga-terminated [23] as well as Sb-stabilized surfaces [Fig. 3(e)]. The positive features are related to

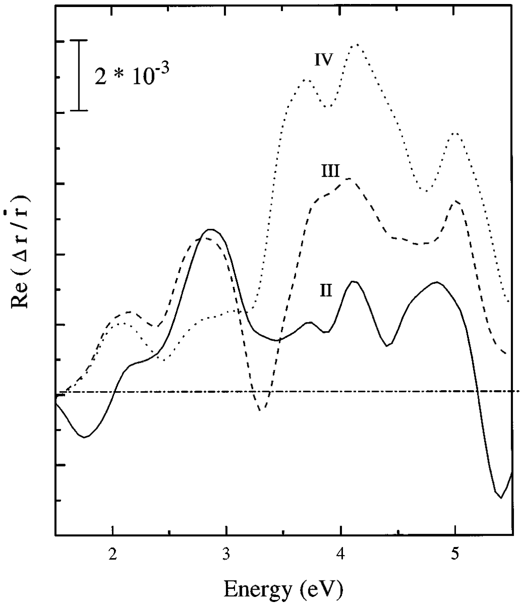

FIG. 4. Calculated RAS spectra for Sb-stabilized (2×4) surfaces for models II, III, and IV. The dashed-dotted line indicates the zero base line.

the existence of group-V surface dimers. Comparing the experimental and calculated spectra for model II we point out that, besides a shift towards lower energy for the calculated spectra with respect to the experimental ones (which is typical for our TB approach, especially at low photon energies), all major experimental features are well reproduced, even in amplitude. Therefore, the comparison of experimental and theoretical results is clearly in favor of model II containing Sb and Ga dimers at the surface.

In conclusion, based on TE calculations and a comparison of measured and calculated RAS spectra, we propose a new model for the Sb/GaAs(100) interface geometry. We suggest a structure characterized by Sb dimers in the outermost layer and a dimerization of the exposed second-layer Ga atoms (model II in Fig. 1). We mention that very recently published scanning tunneling microscopy results have also been interpreted in favor of the coexistence of surface Sb and Ga dimers [28].

Moreover, our results demonstrate that RAS spectra calculated within the TB approximation based on precise structural data reproduce the experimental results very well. This fact in conjunction with the experimental finding of a pronounced dependence of the surface optical anisotropy on microscopic surface properties, such as the bonding of surface atoms in the outermost layer, demonstrates that the microscopic structure of the surface mostly determines the surface optical response. Vice versa, the anisotropic surface optical response supported by appropriate calculations turns thus out to be a valuable tool for determination of the microscopic surface structure.

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