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Photoemission study of GaSb(111) and Ge adsorbed on GaSb(111) surfaces

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Abstract. Clean GaSb(111)A–2 × 2 surfaces, prepared by cycles of ion bombardment and annealing, and GaSb(111)A with various Ge coverages were investigated using low-energy electron diffraction and different modes of photoelectron spectroscopy with synchrotron radiation. Valence band energy distribution curves, and constant-initial-state, and constant-final-state spectra obtained for the clean surface exhibit strong resonances at 19.2 and 19.7 eV which are associated with surface Ga $3d_{5/2}$ and $3d_{3/2}$ core excitons. The amplitudes of the resonances decrease monotonically with increasing adsorbate layer thickness. At a Ge coverage of 1.9 Å the resonances disappear, and concomitant changes in the adsorbate and substrate core-level spectra are observed. The data provide detailed information about the chemical bonding between adsorbate and substrate atoms, and indicate that the growth mode is primarily layer by layer but is not epitaxial.

1. Introduction

The non-polar (110) cleavage surfaces of III–V compound semiconductors are frequently regarded as model systems, and in the past the electronic and geometrical structure of (110) surfaces has been studied extensively. Recently the polar (111) surfaces have attracted increasing interest stimulated by the practical importance of such surfaces. For example, optoelectronic devices are primarily based on the polar surfaces of direct-gap III–V semiconductors.

The Ga-terminated GaSb(111)A surface prepared by ion bombardment and annealing exhibits a 2 × 2 reconstruction. The geometrical structure and registry of the 2 × 2 reconstruction with respect to the bulk crystal were established from surface x-ray diffraction measurements by Feidenhans'l *et al* [1]. In the structural model one Ga atom is missing per 2×2 surface unit cell, which results in a planar geometry with sp^2 hybridization of the Ga atoms similar to that found on the (110) surface. Related reconstructions are found on the InSb(111)A [2], GaAs(111)A [3], and GaP(111)A [4] surfaces. The electronic structure of the (111)A surface has some analogies with the (110) surface, for example the dangling bonds of the cations at the surface are expected to be unoccupied. This has been verified experimentally by both scanning tunnelling microscopy [5] and inverse photoemission spectroscopy [6].

The Ge/GaSb(111)A system with a lattice mismatch of ∼7% is an example of an extremely strained heterostructure. Here we present an investigation, using low-energy electron diffraction and different modes of photoelectron spectroscopy with synchrotron radiation, of the clean GaSb(111)A–2 × 2 reconstructed surface and the room temperature growth of Ge on this surface.

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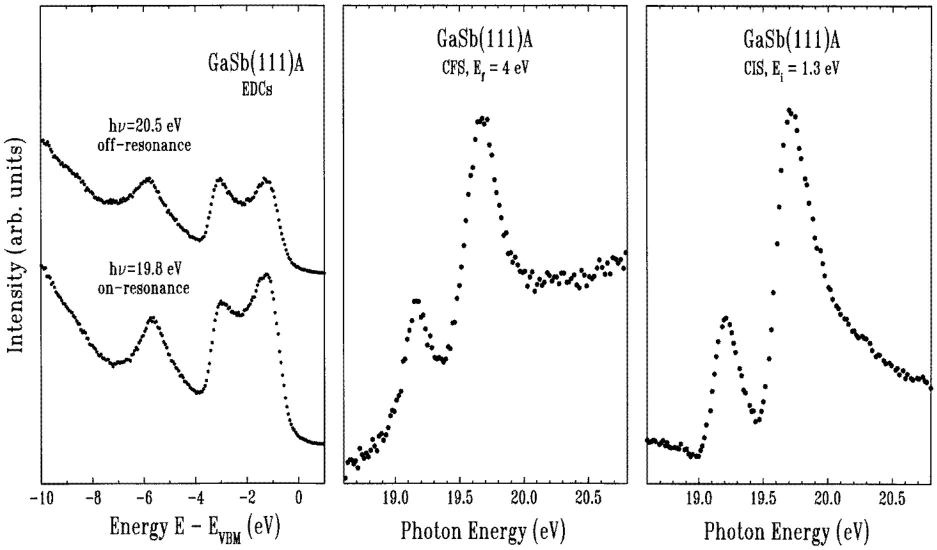

Figure 1. Energy distribution curves recorded at photon energies of 19.8 eV and 20.5 eV, and constant-final-state and constant-initial-state spectra obtained from a clean GaSb(111)A–2 × 2 reconstructed surface.

2. Experimental procedure

The measurements were performed on the FLIPPER II beamline at the Hamburg Synchrotron Radiation Laboratory (HASYLAB) at DESY. The plane grating monochromator covers the photon energy range 15–150 eV with good resolution and very little second-order and stray light. The photoemission chamber is equipped with a low-energy electron diffraction (LEED) system and a double-pass cylindrical mirror electron analyser (CMA). The overall instrumental resolution of the monochromator and electron analyser for these measurements was typically 200 meV.

Clean p-type (undoped, 1.7×10^{17} cm^{-3}) GaSb(111)A surfaces were prepared by ion bombardment followed by annealing until the surface exhibited a sharp (2×2) LEED pattern and the photoemission spectra showed no trace of impurities. The surfaces were exposed at room temperature (RT) to a Ge flux from a Knudsen cell with a PBN crucible. The evaporation rate as monitored with a quartz crystal oscillator was 0.5 Å min^{-1} assuming that the sticking coefficient of Ge on the GaSb surface was equal to that on the quartz crystal.

By using synchrotron radiation one has a tunable source for the primary excitation in photoemission, and in addition to the usual energy distribution curves (EDC) it is possible to record different kinds of spectra. Constant-final-state (CFS) spectra are obtained by sweeping the photon energy while keeping the final energy of the electron analyser E_f constant. For the results presented here we chose a final energy (kinetic energy of the photoelectrons) of 4 eV. The measured variation of the secondary-electron emission is directly correlated with the optical absorption coefficient and it gives information about the joint density of states, similarly to electron energy-loss spectroscopy (EELS) in the core-level transition region. For constant-initial-state (CIS) spectra the photon energy and the energy of the electron analyser are swept synchronously so that the initial-state energy is kept constant. The initial-state energy for the spectra presented here was 1.3 eV below the valence band maximum.

3. Results and discussion

Valence band, and CIS and CFS spectra of a clean GaSb(111)A surface are shown in figure 1. Both CIS and CFS spectra exhibit strong resonances at 19.2 and 19.7 eV photon energy, and in particular the CIS spectrum shows typical asymmetrical Fano line shapes. We interpret the resonances in analogy with the results from GaSb(110) [7, 8] and GaSb(001) [9] surfaces. The enhancement of the primary-electron yield occurs when the photon energy is sufficient to excite transitions from Ga $3d_{5/2}$ and Ga $3d_{3/2}$ core levels to empty conduction band states. The resonances are due to the increase in oscillator strength associated with the formation of localized surface core excitons. The excitons are associated with the empty Ga dangling bonds, which are present on the (111)A surface as has been verified by scanning tunnelling microscopy [5] and inverse photoemission spectroscopy [6]. On the anion-terminated GaAs$(\overline{111})$B surface as shown by Kipp *et al* [10] there are no such resonances, and they concluded that no empty Ga states were present. This was confirmed subsequently by scanning tunnelling microscopy [11].

The decay of the exciton state is responsible for the enhancement, which is also seen in valence band EDCs displayed in figure 1. The spectra were recorded at two different photon energies; the lower curve at a photon energy of 19.8 eV close to the resonance energy (on-resonance), and the upper curve at 20.5 eV, i.e. 0.8 eV above the resonance (off-resonance). The pronounced enhancement in the valence band at the resonance energy can be clearly seen.

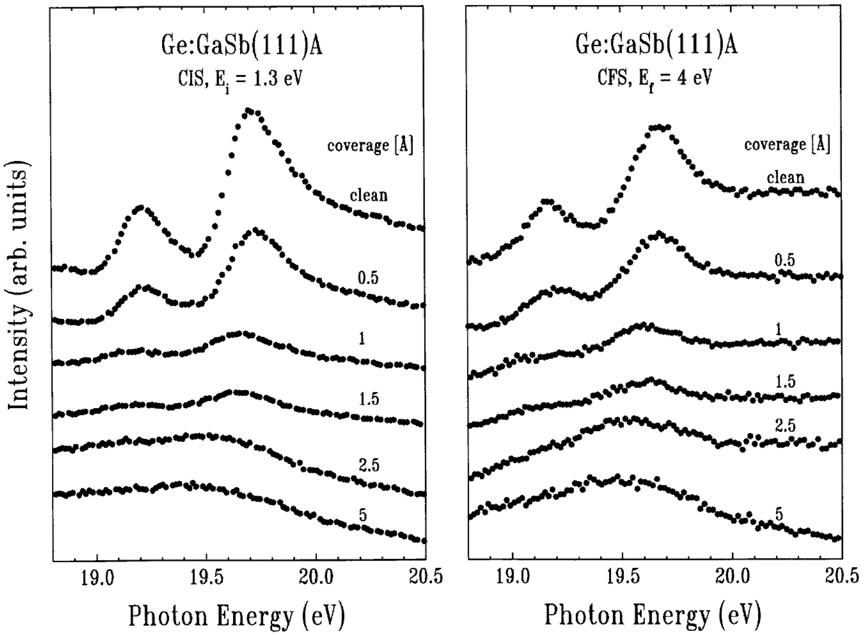

Figure 2. Constant-initial-state and constant-final-state spectra obtained from a clean GaSb(111)A surface and after depositing various Ge coverages.

The cation surface excitons are generated by the cation dangling-bond orbitals at the surface. Since empty cation dangling bonds are only present on the ideal reconstructed surface, the amplitude of the resonance is a very sensitive indicator of the fraction of Ga atoms on the surface. CIS and CFS spectra for various coverages of germanium on GaSb(111)A are shown in figure 2. Both sets of data show that the cation resonances decrease monotonically with increasing adsorbate layer thickness and disappear at a Ge coverage of ~1.9 Å, which confirms the surface character of the observed features. Spectra for higher coverages show only background. The rapid attenuation of the resonances is consistent with the growth mode which was determined, as described below, from the coverage dependence of the core-level intensities.

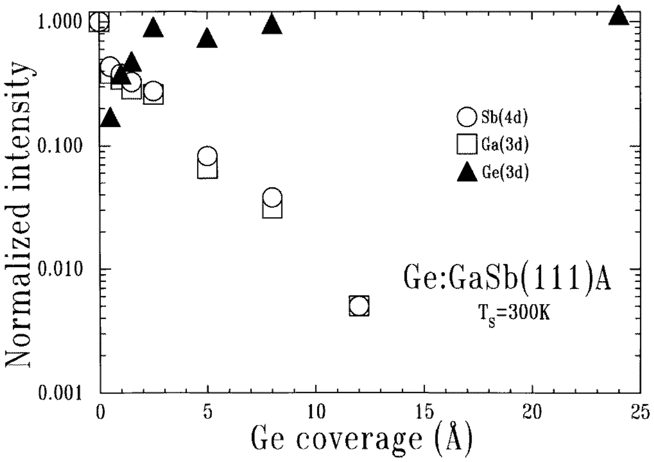

Figure 3. Integrated intensities of the Ga 3d, Sb 4d, and Ge 3d core levels as a function of Ge coverage. The intensities of the substrate peaks are normalized to the clean surface, and the Ge 3d core-level intensities are normalized to a thick Ge film.

Figure 3 shows the intensities of the Ga 3d, Sb 4d, and Ge 3d core levels as a function of Ge overlayer coverage calculated from the core-level energy distribution curves. For these studies a photon energy of 80 eV was used to ensure high surface sensitivity and similar escape depths for the electrons emitted from the Ga 3d, Sb 4d, and Ge 3d core levels. The substrate and adsorbate signals are normalized to the intensities observed from the initially clean surface and a thick Ge layer, respectively. The attenuation profiles of the photoemission intensity as a function of overlayer thickness were obtained from the raw data by subtracting a linear background function and integrating the area under the peaks. The variation of the core-level intensities as a function of coverage provides information about the growth mode. Exponential attenuation of the substrate lines is observed until they disappear, which indicates layer-by-layer growth. The rapid increase in the adsorbate signal during the first stages of growth agrees with this conclusion. The same growth mode was observed for the Ge/GaSb(110) interface [12]. Furthermore, the Ga and Sb signals exhibit the same attenuation rate for all coverages, which indicates that no interfacial reactions take place in which Ga or Sb atoms are liberated.

To get more information about the interface region we performed a curve-fitting analysis of the core-level spectra using approximated Voigt functions [13]. The fitting parameters were adjustable within narrow, physically reasonable, limits, and were optimized using a least-squares minimization, paying attention to the internal consistency of the results for

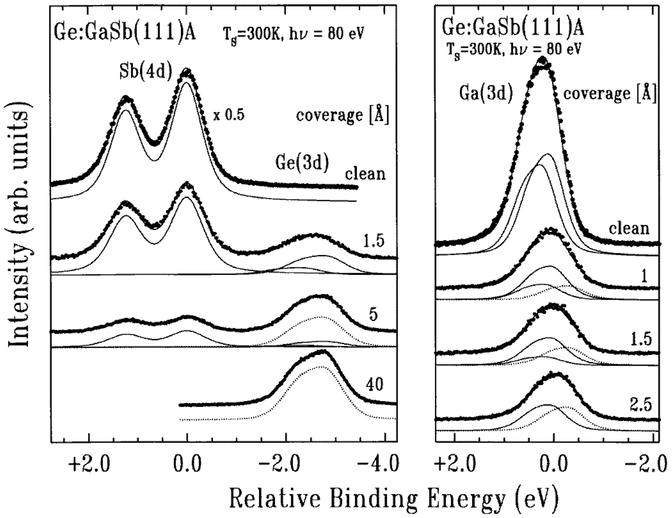

Figure 4. Sb 4d, Ge 3d, and Ga 3d core-level spectra obtained from the clean GaSb(111)A surface and for various Ge coverages. The data were background subtracted and analysed using a curve-fitting procedure to reveal the individual components. The dots represent the experimental data; the solid and dotted curves show the components from the fit and their sum. The energy scale is referenced to the substrate bulk Sb $4d_{5/2}$ component.

different coverages. In figure 4 we show a set of angle-integrated, background-subtracted spectra of Ga 3d core levels recorded for different Ge coverages. The results of the fitting procedure are indicated by solid lines and the data points are marked by dots. The Ga 3d core-level spectra from a clean GaSb(111)A surface exhibit components which can be associated with surface atoms and those in a bulk-like environment. The surface component is shifted by 0.14 eV to higher binding energy. A detailed description of the photoemission results from the clean surface has been published elsewhere [14]. In order to fit the substrate core levels from the adsorbate-covered surface, the same spin–orbit splitting, branching ratio, surface-to-bulk shift and Lorentzian broadening were used as in the case of the clean surface. The intensity of the surface component is rapidly attenuated and disappears at a coverage ∼1.9 Å. The disappearance of the core-level surface component coincides with the disappearance of the resonances in the CIS and CFS spectra, and corresponds to the completion of the first monolayer at a coverage of ∼1.9 Å. Concurrent with the attenuation of the surface component we observe the growth of an additional component (indicated by the dotted curves in figure 4) which is shifted by 0.35 eV to lower binding energy with respect to the bulk peak. We attribute this peak to Ga–Ge bonds from electronegativity considerations. Photoemission investigations on Ge/GaAs(110) by Aldao *et al* [15] show a Ga 3d component shifted by the same magnitude and in the same direction, which they associated with Ga–Ge bonds. The increase in the intensity of the chemical-shifted component and the reduction of the surface component constitute evidence for the interaction of the Ge atoms with the Ga atoms on the surface. At coverages beyond ∼1.9 Å only bulk and chemically shifted components are needed to fit the Ga 3d spectra. The ratio of their intensities is constant, and is the same as the surface-to-bulk ratio of the clean surface, which is consistent with the conclusion that all of the surface Ga atoms bond to Ge atoms at the interface.

Further evidence for Ga–Ge bonding is provided by the changes in the linewidths of the

Ge 3d core-level spectra with increasing coverage. A sequence of background-subtracted Sb 4d and Ge 3d core-level EDCs are plotted in figure 4. The Sb 4d spectra of the clean [14] and Ge-covered surfaces are well described by a single spin–orbit-split doublet. The Ge 3d core levels indicate that the growth process proceeds in two stages. Up to a coverage of $\sim$1.9 Å two components with a separation of 0.49 eV are required to fit the Ge 3d spectra. The ratio of the higher- to lower-binding-energy components is 1:3, which corresponds to the ratio of vacancy sites to Ga atoms on the clean surface. We attribute the lower-binding-energy component to Ge–Ga bonds and the higher-binding-energy component to bonds at the vacancy sites. After the saturation of all Ga atoms and vacancy sites at a coverage $\sim$1.9 Å, the Ge 3d core-level spectra exhibit a third spin–orbit-split component (marked by the dotted curves), which increases with increasing Ge coverage, while the ratio of the other components remains constant and their intensity decreases. This component can be clearly assigned to Ge–Ge bonds. In agreement with previous experiments [16] we find a spin–orbit splitting of 0.585 eV, a Lorentzian linewidth of 0.17 eV, and a branching ratio of 1.5 for the Ge 3d core levels.

The Gaussian widths of the peaks obtained from the fits to the adsorbate spectra are larger than those for the clean surface. We attribute this to the variety of bond angles necessary to reduce the strain at the interface. The rapid attenuation of the surface and bulk LEED reflections with increasing Ge coverage indicates that the interface is not ordered. This is also observed for the room temperature growth of Ge/GaSb(110) [12] and the lattice-matched Ge/GaAs(110) [15] system.

4. Conclusion

We have presented photoemission data for clean GaSb(111)A surfaces which exhibit strong resonances in the photoelectron yield at 19.2 and 19.7 eV, which we attribute to surface Ga 3d core excitons associated with empty Ga dangling-bond states. Our investigation of the growth of germanium on GaSb(111)A at room temperature indicates layer-by-layer growth and chemical bonding between Ge atoms and Ga atoms. The measurements provide evidence for an abrupt but non-ordered interface.

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References

[1] Feidenhans'l R, Nielsen M, Grey F, Johnson R L and Robinson I K 1987 *Surf. Sci.* **186** 499
[2] Bohr J, Feidenhans'l R, Nielsen M, Toney M, Johnson R L and Robinson I K 1985 *Phys. Rev. Lett.* **54** 1275
[3] Tong S Y, Xu G and Mei W N 1984 *Phys. Rev. Lett.* **52** 1693
[4] Xu G, Hu W Y, Puga M W, Tong S Y, Yeh J L, Wang S R and Lee B W 1985 *Phys. Rev.* B **32** 8473
[5] Haberern K W and Pashley M D 1990 *Phys. Rev.* B **41** 3226
[6] Janowitz C, Manzke R, Olde J and Skibowski M 1990 *Proc. 20th Int. Conf. on the Physics of Semiconductors (Thessaloniki, 1990)* vol 1, ed E M Anastassakis and J D Joannopoulos (Singapore: World Scientific) p 207
[7] Eastman D E and Freeouf J L 1975 *Phys. Rev. Lett.* **34** 1624
[8] Faul J, Neuhold G, Ley L, Fraxedas J, Zollner S, Riley J D and Leckey R C G 1993 *Phys. Rev.* B **48** 14 301
[9] Olde J, Behrens K-M, Barnscheidt H-P, Manzke R and Skibowski M 1991 *Phys. Rev.* B **44** 6312

[10] Kipp L, Barnscheidt H-P, Janowitz C, Mante G, Olde J, Manzke R and Skibowski M 1990 *Solid State Commun.* **75** 839

[11] Biegelsen D K, Bringans R D, Northrup J E and Swartz L-E 1990 *Phys. Rev. Lett.* **65** 452

[12] Mönch W 1984 *Festkörperprobleme (Advances in Solid State Physics)* vol 24, ed P Grosse (Braunschweig: Vieweg) p 229

[13] Wertheim G K, Butler M A, West K W and Buchanan D N 1974 *Rev. Sci. Instrum.* **45** 1369

[14] van Gemmeren T and Johnson R L 1997 *Surf. Sci.* at press

[15] Aldao C M, Vitomirov I M, Xu F and Weaver J H 1989 *Phys. Rev.* B **40** 3711

[16] Le Lay G, Kanski J, Nilsson P O, Karlsson U O and Hricovini K 1992 *Phys. Rev.* B **45** 6692
Bringans R D, Olmstead M A, Uhrberg R I G and Bachrach R Z 1987 *Phys. Rev.* B **36** 9569