Electronic structure of Sb overlayers on GaAs(110)

Monika Mattern-Klosson, R. Strümpler, and H. Lüth

*II. Physikalisches Institut der Rheinisch-Westfälischen Technischen Hochschule Aachen,
D-5100 Aachen, Federal Republic of Germany*

Sb overlayers deposited at 300 K on GaAs(110) surfaces cleaved in ultrahigh vacuum have been investigated by ultraviolet and x-ray photoemission and ellipsometric spectroscopies. For the strongly chemisorbed, well-ordered first monolayer of Sb (1×1 as determined by low-energy electron diffraction) information about electronic interface states and optical transitions between them is obtained. On top of this first Sb layer a semiconducting Sb species is deposited. The metallic character of the film, revealed by a sharp Fermi edge in the ultraviolet photoemission spectra, occurs not before evaporation of about 20 monolayers of Sb. Simultaneous measurement of the work function gives further information about electronic states in the Sb overlayer. The results can also be explained consistently with respect to the recently measured Schottky barriers on GaAs(110)-Sb.

I. INTRODUCTION

For a deeper understanding of Schottky barriers on semiconductors a detailed knowledge about the morphology, the crystallographic structure, and the electronic properties of the metallic overlayers is necessary. Even if an essential part of the barrier height on a III-V compound semiconductor surface is already established after deposition of tiny fractions of a monolayer, the final band bending below a "thick" film with metallic properties might be due to different mechanisms.[1,2] It will definitely also be influenced by the "bulk electronic properties" of the metal overlayer.

In the context of these problems the overlayer system of Sb on GaAs(110) is of particular interest. From recent low-energy electron-diffraction (LEED) structural analysis and from Auger-electron spectroscopy[3] it is known that Sb grows on cleaved GaAs(110) surfaces, at least in two different modifications. A first well-ordered monolayer is strongly chemisorbed. On top of this layer Sb is deposited without any long-range order and with a weaker chemical bond. For the first monolayer, theoretical structure models exist, which place the Sb atoms at positions so as to continue a nearly unreconstructed GaAs lattice.[4] Furthermore, the Schottky-barrier height has been measured by uv photoemission spectroscopy (UPS) for Sb coverages up to 25 monolayers (ML).[5] Because of all these available data, GaAs(110)-Sb should be an ideal model system for studying also the change of the electronic properties from the first epitaxially grown atomic layer up to the bulk states of metallic Sb. UPS and x-ray photoemission spectroscopy (XPS) as well as ellipsometric spectroscopy are used in this work to get information about electronic states at the interface and within thicker Sb layers.

II. EXPERIMENTAL

The measurements were performed on (110) surfaces of n-type [Te-doped, $n \simeq (1-5) \times 10^{17}$ cm^{-3}] and p-type [Zn-doped, $p \simeq (1-5) \times 10^{17}$ cm^{-3}] GaAs single crystals. The surfaces were prepared by cleavage using the double wedge technique in ultrahigh vacuum (UHV) systems pumped by ion pumps and Ti sublimators ($p < 10^{-8}$ Pa). High-purity Sb was evaporated from an electrically heated Mo basket with an arrival rate of Sb atoms at the crystal surface (300 K) of about 0.6 ML/min. One monolayer contains 8.85×10^{14} atoms/cm^2 referred to the GaAs(110) surface. The evaporation rate was controlled by a quartz balance.

In the UPS measurements a differentially pumped discharge lamp was used as source for the He I (21.2 eV) and He II (40.8 eV) radiation. The photoelectrons were detected under normal emission by means of a hemispherical electron-energy analyzer (resolution $\Delta E \simeq 0.1$ eV). The same analyzer was also used in the XPS measurement, but with the resolution set to about 0.75 eV. For XPS an x-ray source with an Al-coated anode was directly mounted on the UHV chamber. All measurements were thus performed with the Al $K\alpha$ line (energetic width $\simeq 0.8$ eV). The system was further equipped with LEED optics in order to check the crystallographic surface structure.

The ellipsometric spectra were taken in a separate UHV chamber with a manual null ellipsometer outside the vacuum such that difference measurements were made through Pyrex windows. Usually the ellipsometric angles Δ and Ψ were determined on the clean surface, after deposition of Sb, in steps of 0.1 eV photon energy. More experimental details are given elsewhere.[6,7]

III. RESULTS AND DATA ANALYSIS

A series of electron-energy distribution curves (EDC's), taken on the cleaved (110) surface of an n-doped GaAs crystal with increasing Sb coverage, is shown in Fig. 1. Upon Sb deposition, a new adsorbate characteristic feature arises in the spectral range of the valence-band maximum (VBM) for a coverage above 0.3 ML. This shoulder appears at 0.74 eV below the Fermi energy E_F

on n-type GaAs and at 0.53 eV below E_F on p-type GaAs. In the coverage range of several monolayers, a broad, washed-out emission maximum develops below the Fermi level [Fig. 1(d)] which gradually replaces the sharp substrate structures. Photoemission from the Fermi edge can be observed for coverages of about 20 ML. At the same time the spectral shape changes into the characteristic form of Fig. 1(e) with sharp emission maxima at 0.8, 1.6, and 2.4 eV below E_F.

The change of the work function $\Delta\phi$ upon Sb deposition is equal to the shift of the low-energy emission onset of the UPS spectra. Figure 2 shows the results for surfaces of n-type GaAs without any band bending before evaporation of Sb and for surfaces of p-type GaAs with an initial depletion layer of -0.3 eV. The values of band bending at the clean surface were determined from the EDC's by means of the energy difference between the Fermi level and the VBM. These energies are given by the intersection between the energy axis and the straight line approximating the EDC's in the concerned spectral range. More details about Sb-induced band bending have been published elsewhere.[5] It should be noted that on n-doped samples the saturation value of $\Delta\phi$ is reached for an Sb coverage of 1.5 ML. On p-type GaAs, however, a further decrease of about 0.1 eV occurs up to 7 ML of Sb.

Further information about the electronic properties of the Sb overlayers is obtained from XPS. The kinetic ener-
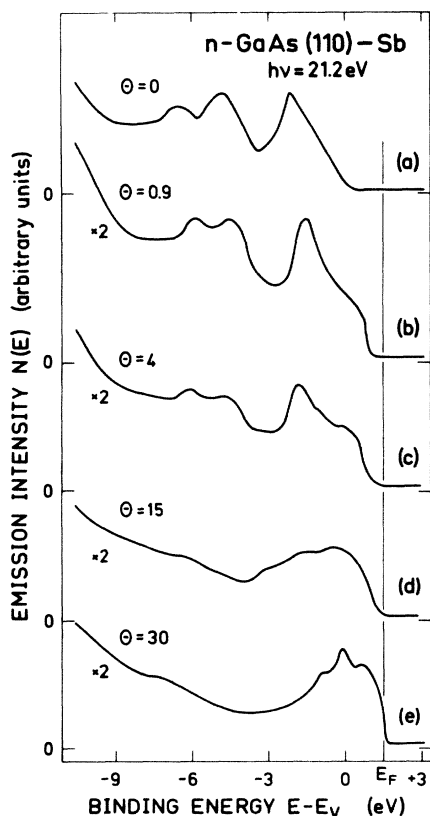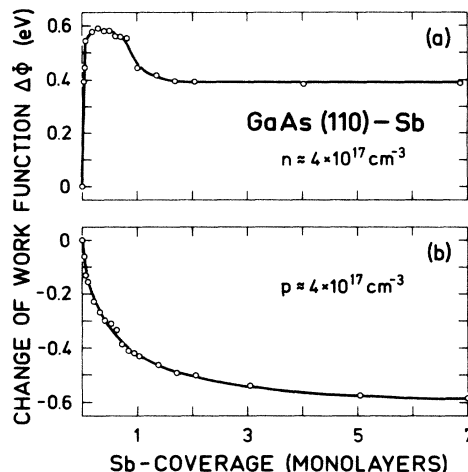
FIG. 2. Sb-induced change of work function $\Delta\phi$ on the (110) surfaces of n-type GaAs (a) without any band bending at the clean surface and of p-type GaAs (b) with an initial depletion of -0.3 eV.

gy of the photoelectrons from the $3d$ core levels ($\simeq 950$ eV) of the adsorbate decreases with coverage in the submonolayer range. Then an increase of about 0.4 eV occurs until saturation is reached at 15 ML of Sb (Fig. 3). Additionally, the full width at half maximum of the $3d$ core-level lines decreases between 0.1 and 2 ML of Sb monotonically by about 0.4 eV to a value determined by the experimental resolution.

Finally, the results of ellipsometric spectroscopy are given in Fig. 4. From the changes of the ellipsometric angles Δ and Ψ upon deposition of 0.5 ML of Sb, effective dielectric functions Reϵ and Imϵ for the Sb overlayer were calculated within a "one-layer" model for photon energies between 1.5 and 4 eV (circles).[6,8] These curves, although formally attributed to the overlayer, not only characterize the adsorbed layer but also still reflect adsorbate-induced changes of the dielectric constants of the substrate. Due to the Franz-Keldysh effect,[9] a change of band bending at the GaAs surface influences its dielectric properties, especially in the spectral range of interband transitions. In

FIG. 1. Electron-energy distribution curves of a clean surface (a) and of Sb-covered [(b)—(e)] (110) surfaces of n-type GaAs taken with He I radiation in normal emission. The binding energy is referred to the energetic position E_v of the valence-band maximum at the clean surface.
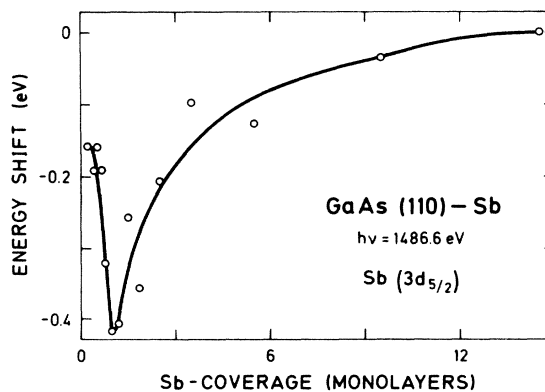
FIG. 3. Energy shift of the $3d_{5/2}$-photoemission line of Sb versus Sb coverage on a cleaved GaAs(110) surface. The curve was measured with the Al $K\alpha$ line.
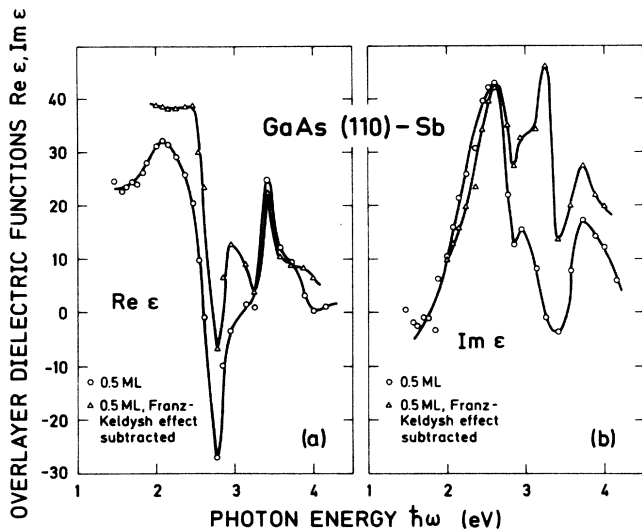
FIG. 4. Overlayer dielectric functions Reϵ and Imϵ versus photon energy of half a monolayer of Sb on an n-type GaAs(110) surface before (O) and after ($\triangle$) correction for the Franz-Keldysh effect in the GaAs space-charge layer.

this case, however, an appropriate correction for the influence of band bending on the dielectric functions is possible. The value of band bending after evaporation of 0.5 ML of Sb on an n-type GaAs(110) surface[5] agrees with that observed after an oxygen dosage of about 1 L.[10] As the oxygen-induced changes of the ellipsometric angles Δ and Ψ can be interpreted only in terms of the Franz-Keldysh effect,[7] they can be used to correct the curves of $\delta\Delta$ and $\delta\Psi$ obtained after Sb deposition for the effects of band bending. As expected, the influence of this correction on the dielectric function of the overlayer decreases with increasing coverage. The corrected curves for Reϵ and Imϵ (triangles in Fig. 4) then characterize only the Sb overlayer. Reϵ exhibits prominent maxima near photon energies of 3 and 3.5 eV; the maxima in Imϵ occur at energies of 2.65, 3.2, and 3.75 eV (average values from several measurements).

IV. DISCUSSION

Since the first monolayer of Sb forms a well-ordered overlayer on the GaAs substrate,[4] its electronic properties are determined by a two-dimensional band structure. Hence, in this coverage range the adsorbate is character-

ized by sharp features in the uv-photoemission and the ellipsometric spectra. The pronounced Sb-induced shoulder at the VBM in the EDC's (Fig. 1) can be related to electronic states of the adsorbed layer, which have been determined theoretically by means of tight binding[11] and self-consistent pseudopotential calculations[12] for 1 ML of Sb on a GaAs(110) surface. These states have also been observed in other regions of the Brillouin zone and with different photon energies.[13,14] Beside two bands, S_5 and S_6, of occupied states at the VBM , theory predicts two bands, S_7 and S_8, of empty states near the conduction-band minimum. Interband transitions between these states should determine the overlayer dielectric functions Reϵ and Imϵ which differ completely from that of polycrystalline Sb.[15] While Reϵ and Imϵ of metallic Sb increase and decrease monotonically with photon energy, respectively, the curves for 0.5 ML of Sb on GaAs(110) exhibit several prominent structures. Table I compares the energetic positions of the maxima of Imϵ from this work with values of the interband transition energies at some points of the Brillouin zone according to Refs. 11 and 12. Since the accuracy of the calculation is limited to ±0.5 eV,[16] however, the agreement between the experimentally and the theoretically determined transition energies must not be taken too seriously. Furthermore, the optical transition-matrix elements are still unknown, so that an association of the peaks of Imϵ with certain transitions in the Brillouin zone seems somewhat arbitrary. It is at least difficult, with the present state of knowledge, to favor one or the other theoretical approach[11,12] purely on the basis of the ellipsometric data.

According to UPS and ellipsometric spectra, the first monolayer of Sb clearly has semiconducting properties. The metallic character of the overlayer does not develop before a film thickness of 20 ML is reached. Then, photoemission at the Fermi edge occurs and the form of the UPS spectra corresponds to that of metallic Sb.[17] No LEED patterns can be seen on the surfaces of these films;[3] they seem to be polycrystalline, as the transverse optical phonon of the Sb overlayer can be detected by means of Raman spectroscopy.[18] The TO phonon disappears for a coverage below 10 ML so that a disordered atomic configuration is given. Accordingly, the adsorbate-derived features in the UPS spectra are very broad and structureless (Fig. 1).

An astonishing result, which has to be explained, is the different behavior of the work function on n- and p-doped material, in particular, for higher coverages (Fig. 2). We

TABLE I. Comparison of the energetic positions of the maxima of the overlayer dielectric function Imϵ for 0.5 ML of Sb on (110) surfaces of n-type GaAs with theoretically determined optical transition energies at symmetry points of the surface Brillouin zone according to Refs. 11 and 12. Imϵ was corrected for the Franz-Keldysh effect in the space-charge layer.

Energies of the maxima of Imϵ in meV (this work)	Transition energies according to Ref. 11 in eV				Transition energies according to Ref. 12 in eV	
	$\overline{\Gamma}$	$\overline{X}$	$\overline{M}$	$\overline{X}'$	$\overline{X}$	$\overline{M}$
2.65	2.0	2.6	2.5	2.4	1.8	2.8
3.2	2.5	3.35	3.25	2.9	2.0	
	3.0	2.9	2.9	2.8	2.15	3.2
3.75	3.5	3.7	3.6	3.35	2.4	

will show that the decrease of the work function $\Delta\phi$ observed only on p-type GaAs for coverages above 1 ML can be interpreted in terms of the gradual change of the electronic structure of the Sb overlayer. For coverages below 1 ML, $\Delta\phi$ is determined by changes of the band bending and the electron affinity at the semiconductor surface and by a contribution due to a dipole moment between substrate and adsorbate. When the first atomic layer of the adsorbate is closed, the electronic structure of the overlayer becomes essential. Changes of the dipole moment at the surface of the Sb film, however, must be independent of the doping of the GaAs substrate so that they should influence $\Delta\phi$ at Sb layers on n- as well as on p-type GaAs in the same way. Furthermore, a shift of the energy levels of the Sb film relative to the Fermi energy might be responsible for the work-function decrease on p-type GaAs. As can be seen from the energetic position of the adsorbate-derived shoulder at the VBM in the UPS spectra [Fig. 1(b)], the electronic states of the Sb film are by 0.2 eV closer to the Fermi energy on p-type GaAs than on n-type GaAs for a coverage of about 1 ML. This is a consequence of the fact that the pinning positions of the Fermi level within the bandgap of GaAs differs by 0.2 eV in both cases, at least up to coverages of about 25 ML.[5] For thick metallic films, however, the energy of the Sb states relative to E_F, i.e., the metal work function being the energetic distance between the vacuum level and the Fermi energy, is independent of the substrate doping and of properties of the interface. In the intermediate coverage range, therefore, an energetic adjustment must occur. Since the work function of Sb overlayers on n-type GaAs remains constant while the value on p-doped samples decreases, donor-type states of the Sb film might be responsible. They could be above E_F, i.e., positively charged, on p-type GaAs, and below E_F, i.e., electrically neutral, on n-type GaAs. According to Fig. 5, they may originate from the gradually developing bulk density of states of metallic Sb. The Madelung energy of the ion cores, as well as the energy of interaction with the valence electrons, may thus depend on film thickness. For the sub-monolayer coverage range, additionally, the strong chemical bond to the substrate should be considered. Chemically inequivalent adsorption sites on gallium and arsenic atoms might be responsible for the broadening of the photoemission line and for the shift of the point of maximum intensity.

V. CONCLUSION

The present study is of particular interest with regard to recent work,[5] where we could show that the Schottky
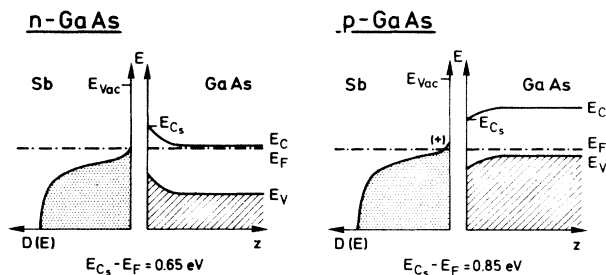

FIG. 5. Energy-level diagram of GaAs and schematic density of states of the Sb overlayer for n- and p-type GaAs for a coverage above 1 ML. The interface states responsible for the band bending are not shown. In both cases the value of the barrier height, i.e., the difference between the energy of the conduction-band minimum at the interface E_{c_s} and the Fermi energy E_F, is indicated.

barrier both on p- and on n-type GaAs is essentially completed after a tenth of a monolayer of Sb and that it does not significantly change anymore up to coverages of about 25 ML. In this whole coverage regime three electronically different Sb species are revealed here; especially, the true metallic character of Sb is reached "very slowly," at coverages of about 20 ML. For thinner films the semi-conducting character of the overlayer prevails. The value of band bending, however, is not influenced by this structural rearrangement. No additional shielding of the charge in the interface states by the metallic overlayer, or in metal-induced gap states (MIGS), changes the barrier height.[1,2] This might be due to the persistence of a semi-conducting Sb interlayer between the GaAs surface and the metallic Sb phase. In future theoretical work on the influence of the metallic overlayer on the Schottky barrier such multiphase structures as found here should, therefore, also be taken into account.

ACKNOWLEDGMENTS

[1]A. Zur, T. C. McGill, and D. L. Smith, Phys. Rev. B 28, 2060 (1983).
[2]J. Tersoff, Phys. Rev. Lett. 52, 465 (1984).
[3]J. Carelli and A. Kahn, Surf. Sci. 116, 380 (1982).
[4]C. B. Duke, A. Paton, W. K. Ford, A. Kahn, and J. Carelli, Phys. Rev. B 26, 803 (1982).
[5]M. Mattern-Klosson and H. Lüth, Solid State Commun. 56, 1001 (1985).
[6]R. Matz and H. Lüth, Appl. Phys. 18, 123 (1979).
[7]R. Dorn and H. Lüth, Phys. Rev. Lett. 33, 1024 (1974).
[8]F. L. McCrackin, E. Passaglia, R. R. Stromberg, and H. L. Steinberg, J. Res. Natl. Bur. Stand. 67A, 363 (1963).

[9]W. Franz, Z. Naturforsch. Teil 13, 484 (1958); L. V. Keldysh, Zh. Eksp. Teor. Fiz. 33, 1022 (1958). Sov. Phys.—JETP, 6, 785 (1958).

[10]W. E. Spicer, I. Lindau, P. E. Gregory, C. M. Garner, P. Pianetta and P. W. Chye, J. Vac. Sci. Technol. 13, 780 (1976).

[11]C. Mailhot, C. B. Duke, and D. J. Chadi, Phys. Rev. B 31, 2213 (1985).

[12]C. M. Bertoni, C. Calandra, F. Manghi, and E. Molinari, Phys. Rev. B 27, 1251 (1983).

[13]P. Skeath, C. Y. Su, W. A. Harrison, I. Lindau, and W. E. Spicer, Phys. Rev. B 27, 6246 (1983).

[14]J. R. Myron, J. Anderson, and G. J. Lapeyre, *Proceedings of the 17th International Conference on the Physics of Semiconductors, San Francisco, 1984*, edited by J. D. Chadi and W. A. Harrison (Springer, New York, 1985).

[15]D. E. Aspnes, Phys. Rev. B 12, 4008 (1975).

[16]C. Mailhot (private communication).

[17]L. Ley, R. A. Pollak, S. P. Kowalczyk, R. McFeely, and D. A. Shirley, Phys. Rev. B 8, 641 (1973).

[18]W. Pletschen, N. Esser, J. Geurts, W. Richter, (unpublished).
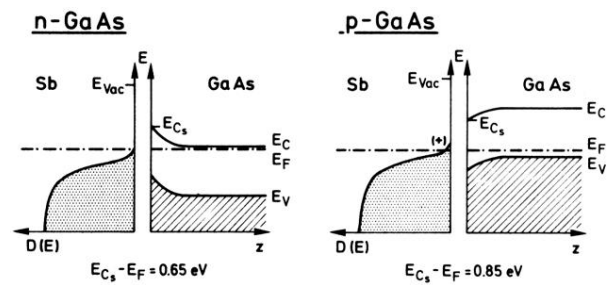
FIG. 5. Energy-level diagram of GaAs and schematic density of states of the Sb overlayer for n- and p-type GaAs for a coverage above 1 ML. The interface states responsible for the band bending are not shown. In both cases the value of the barrier height, i.e., the difference between the energy of the conduction-band minimum at the interface E_{c_s} and the Fermi energy E_F, is indicated.