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Valence band offset in ZnS layers on Si(111) grown by molecular beam epitaxy

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The heterojunction between silicon(111) and zinc sulfide was studied using Auger electron spectroscopy, photoelectron spectroscopy, and low-energy electron diffraction. Zinc sulfide layers were deposited onto cleaved Si(111) surfaces as well as Si(111)-(7×7) wafers by molecular beam epitaxy. The overlayers exhibited fair crystalline quality, and the characteristic valence-band spectrum of ZnS. The valence-band offset between the two semiconductors was determined from the core and valence-band spectra ($\Delta E_v = -0.7$ eV) and found to be much smaller than predicted. We attribute this disagreement, and the larger than usual scatter in our data, to the influence of interface dipoles in this polar interface, the density of which may partly be influenced by a varying amount of interface reaction.

I. INTRODUCTION

The experimental investigation of heterojunction formation is important for an understanding of the factors governing their physical properties. Among these, the valence- and conduction-band offsets are the most important ones, since they dominate the transport properties across the interface.¹ Photoemission studies of interface formation and band offsets performed over the last decade have shown that this technique may be used to determine band offsets with reasonable precision, and new insights have been gained.² Such studies have also been useful as a testing ground for the various theories aimed at describing the observed band offsets. Many heterojunction interfaces involve two species with different lattice constants, such that strain effects on the band structure of one of the semiconductors become important. Lattice-matched junctions do not present these problems, and are therefore most suitable as models for the study of such systems at a fundamental level, for example through self-consistent supercell calculations.^{3,4} Many such heterojunctions have been investigated both experimentally and theoretically. While some of these are of more academic interest, some also may find applications. The heterojunction system discussed in the present paper, zinc sulfide on silicon(111), may be among the latter, since it holds promise in future devices combining silicon logic circuits with optoelectronics. It offers a low lattice mismatch between the two semiconductors ($\Delta a/a = 0.4\%$). We have grown ZnS on cleaved Si(111)-(2×1) as well as Si(111)-(7×7) wafer surfaces using *in situ* molecular beam epitaxy (MBE), and studied the growth as well as the electronic structure of the heterojunction using Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and core- and valence-level photoemission with synchrotron radiation. We compare our results with calculations for the valence-band offset ΔE_v , and discuss the special implications of growing the polar (111) surface of ZnS on Si for the magnitude of the band offset. Such polar interfaces lead to the occurrence of large interface dipoles if all atoms are located at their proper lattice sites; however, there may be deviations from such an ideal arrangement because the large electric fields may induce migration of atoms across the interface, causing a par-

tial reduction of the dipole.⁵ Recent theoretical models indicate that at a polar interface between heterovalent semiconductors the band offsets should indeed depend on the microscopic arrangement at the interface.⁵⁻⁸

II. EXPERIMENT

The experiments were carried out in three separate chambers. The growth of ZnS and the low-energy electron diffraction (LEED) pattern of the ZnS layers were examined in an ultrahigh vacuum chamber equipped with an Auger electron spectrometer (Perkin-Elmer Inc.) and a four-grid LEED optics (VG Scientific Ltd.). All chambers were equipped with a crystal holder allowing sample heating for cleaning purposes, and with a single MBE cell of our own design, which was filled with high purity ZnS powder, and run at a temperature of between 720 and 800 °C during layer preparation. Previous studies have shown that ZnS layers can be grown by MBE⁹ using a single cell.

The photoemission experiments were carried out on the toroidal grating monochromator (TGM) beamlines TGM 5, TGM 6, and the plane grating monochromator beamline HE-PGM 2 of the BESSY (Berliner Elektronen-Speicher-Gesellschaft für Synchrotronstrahlung) storage ring in Berlin. While the TGM beamlines gave access to a high flux of photons with good resolution but a photon energy range limited to the excitation of the Si 2*p*, Zn 3*d* and the valence levels, the HE-PGM 2 line provided light at higher photon energies suitable for the sulfur 2*p* level but inferior resolution. A commercial angle-resolved photoelectron spectrometer (ARIES HA 50 by VSW Ltd., GB) was used for the studies with lower energies, while an angle-integrating energy analyzer (HA 100 by VSW Ltd.) was employed for the studies of interface reactions using higher photon energies. All ultrahigh vacuum chambers had base pressures of 5×10^{-11} – 1×10^{-10} mbar. Si wafers (*n* type, 2 Ω cm, from Wacker Chemitronic, Germany) were cleaned by an outgassing/heating procedure in which the crystal was briefly heated to about 1000 °C after prolonged outgassing at 550–600 °C. The Si(111)-(2×1) surfaces were cleaved from prenotched bars of *n*-type Si. Substrate temperatures during ZnS evaporation were between 300 and 600 K.

III. RESULTS AND DISCUSSION

A. ZnS overlayer growth characterization

In a first step, the growth of ZnS was investigated using AES. The Zn *MNN*, S *LMM* and Si *LMM* lines were used in order to establish the growth mode. For substrate temperatures above 600 K only a saturation of the sulfur signal was found, while the Zn line remained very weak, excluding an epitaxial growth of ZnS. This points to a drastic reduction of the sticking coefficient for zinc above this temperature, which has also been found by Yokoyama *et al.*¹⁰ In Fig. 1 we show the relative intensities of the Si substrate and the ZnS overlayer for the lower temperatures eventually found to be most suitable for thick overlayer growth. The intensity of the Si *LMM* signal quickly decreases up to about one monolayer and then exhibits an exponential trend, indicating layerwise growth after the first monolayer. In order to ascertain that the compound semiconductor ZnS rather than Zn and sulfur clusters grow on the substrate under these conditions, we have carried out annealing experiments up to temperatures of 500 °C following the growth of thick (~100 to 200 Å) layers. No change in the relative intensities of Zn and S lines was found; if only clusters of the elements were present, the large divergence in vapor pressures of these elements would cause a large difference in those intensities. The stoichiometry of the ZnS layers grown on Si(111) was also tested by x-ray photoelectron spectroscopy using a laboratory AlK α x-ray source. The relative intensities of the Zn 3*d* and S 2*p* core-level lines were recorded for thick overlayers on silicon as well as a specimen of the ZnS powder used in the MBE cell; they were found to be equal to within the noise level for the two specimens.

While these data demonstrate that the ZnS compound semiconductor actually grows on the silicon surface, the structural modification of the overlayer needs additional confirmation. ZnS may crystallize in different conformations as a function of growth temperature and pressure; under conditions of low pressure and temperatures below 1020 °C the zinc blende structure, with a lattice constant of 5.409 Å, is the most stable one.¹¹ Figure 2 shows the LEED

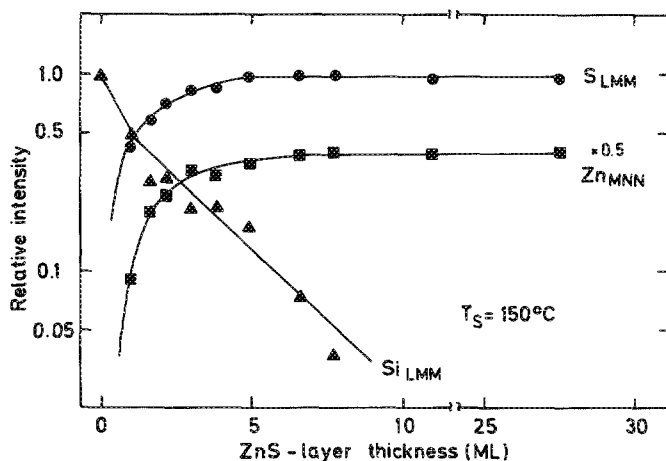


FIG. 1. Relative intensity of the substrate (Si *LMM*) and overlayer (S *LMM* and Zn *MNN*) Auger peak heights as a function of overlayer thickness recorded on a cleaved Si (111) surface at a substrate temperature of 150 °C.

patterns of a freshly cleaved Si(111) surface (top) with the characteristic (2×1) reconstruction spots. Upon evaporation of a small amount of ZnS this reconstruction is removed, and the (1×1) pattern is observed; the corresponding diffraction pattern, with clearly broadened spots, is shown in the center of Fig. 2. The final pattern of a thick (50 ML) layer of ZnS again displays a (1×1) pattern, but with strongly broadened spots, indicative of a degraded crystalline quality in the overlayer. While the LEED patterns indicate that there are probably a large number of defects in the overlayer, the existence of the pattern in itself is proof that

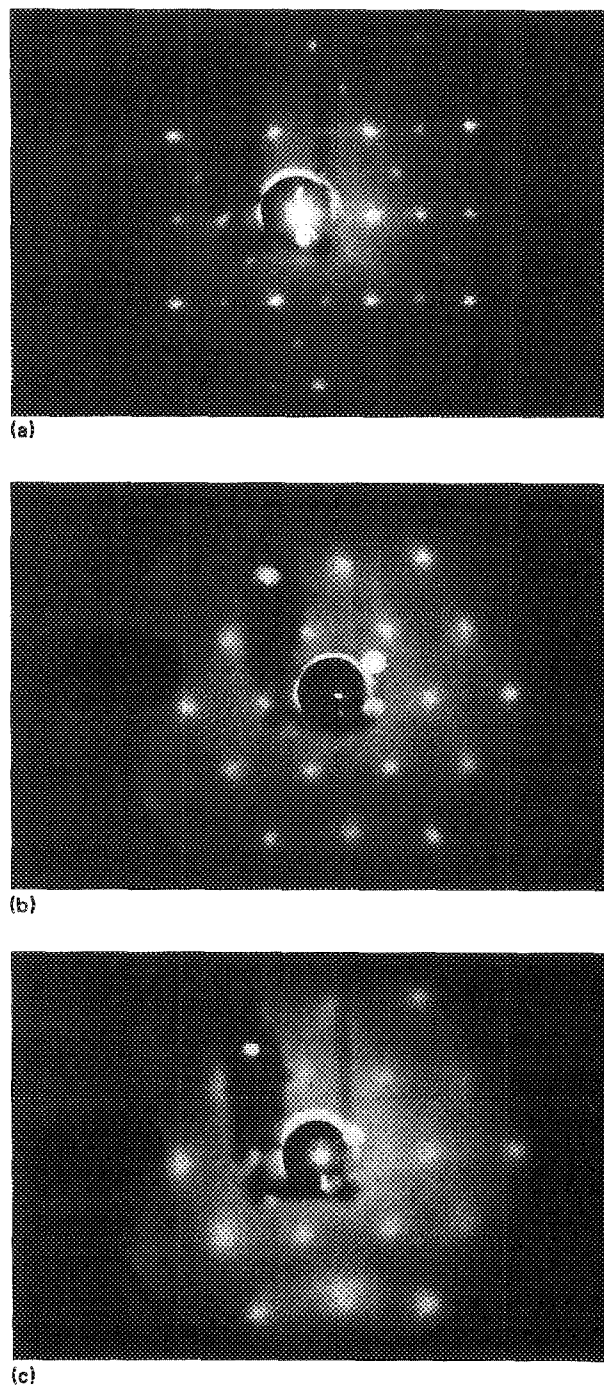


FIG. 2. LEED diffraction patterns recorded from (a) a clean cleaved Si (111) (2×1) surface, (b) a 0.2-ML ZnS layer, (c) a 50-ML ZnS layer, grown at a substrate temperature of 150 °C.

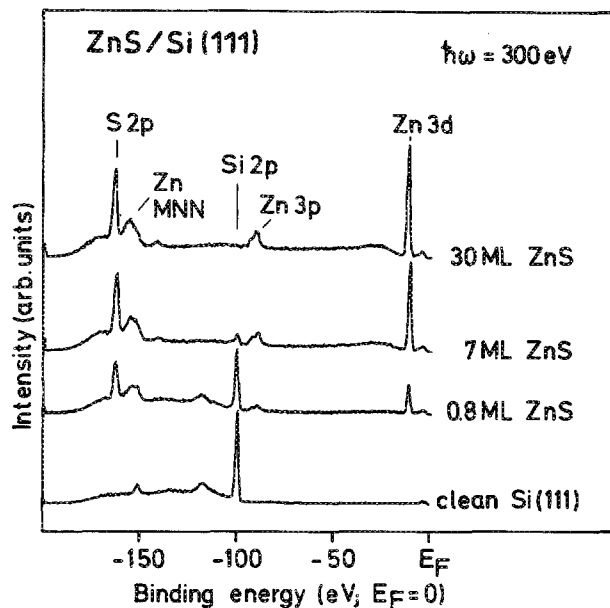


FIG. 3. Photoelectron spectra of a clean Si (111) surface, and different depositions of ZnS, recorded in normal emission, at a photon energy of 300 eV.

crystalline ZnS overlayer growth prevails, most likely in the zinc blende structure, with a (111) crystal orientation.

The growth of ZnS on Si(111) was also investigated using core level photoemission. A sequence of overview spectra, recorded *in situ* after each deposition step, is shown in Fig. 3. The photon energy of 300 eV was chosen in order to observe core level emission from all elements involved. The bottom spectrum shows the spectra of the clean Si(111) surface, displaying the sharp Si 2*p* line and the less intense Si *L*VV Auger and Si 2*s* lines going to higher binding energies. Upon deposition of ZnS, the Si 2*p* intensity decreases, and the S 2*p* and Zn 3*d* as well as the less intense Zn 3*p* and Zn *L*M*M* Auger lines increase. For small amounts of ZnS the intensity of the S 2*p* line actually increases more rapidly than the Zn 3*p* line. This behavior, and the rapid decrease of the Si *L*VV Auger line up to about one monolayer deposition, was observed at every experiment, independently of overlayer growth temperature. We interpret this behavior as due to a preferential adsorption of sulfur on the silicon surface, and the subsequent bonding of the Zn atoms to the adsorbed sulfur atoms. This behavior has also been found in studies of interface formation between other elemental and compound semiconductors. For the widely studied case of GaAs on silicon, a strongly bonded monolayer of arsenic is usually found on the Si substrate.¹² For ZnSe on Si(100) which probably is the closest analogue to the system described here, Bringans *et al.* found that Si—Se bonds occurred at the interface.¹³

In previous studies of heterojunction formation involving II—VI semiconductors, we have found clear evidence for interface reactions.¹⁴ There is ample evidence that layers intentionally deposited at the interface,¹⁵ and therefore probably also reacted layers, can influence the magnitude of the valence-band offset. We have thus focused on this question also in the present study. High-resolution core-level photoe-

mission is one of the most suitable techniques for the study of such reactions in view of its sensitivity, although it must be noted that the information contained in the core-level line shape is sometimes difficult to extract and often rather un-specific. Consider the shape of the Si 2*p* core level shown for different coverages of ZnS in Fig. 4. The bottom spectrum shows the clean surface Si(111)-(2×1) 2*p* core level. Superimposed on the data points is the curve resulting from our line-shape analysis, based on emission from Si bulk atoms. The line-shape analysis uses Lorentzian lines representing the intrinsic linewidth, convoluted by Gaussians in order to take into account the finite monochromator and electron analyzer resolution as well as additional intrinsic broadening, e.g., by phonons; the parameters are optimized based on a nonlinear least-squares routine utilizing the Marquardt algorithm.¹⁶ At the photon energy which we have used (116 eV), emission from bulk Si atoms dominated the spectrum; at higher photon energy, e.g., 136 eV, the surface emission¹⁷ becomes quite prominent. Upon deposition of ZnS, the intensity decreases (see curves in Fig. 4), but the shape of the lines hardly changes, such that for this surface, interface reaction seems to be less important. The situation is different for the Si(111)-(7×7) surface which was studied in a different set of experiments. Here, a second line in the Si 2*p* region was found upon deposition of ZnS, shifted towards higher binding energy by about 1.5 eV with respect to the bulk Si emission. If we take into account the electronegativities of the two atoms (Pauling's¹⁸ values are $\chi_{\text{Si}} = 1.8$ and

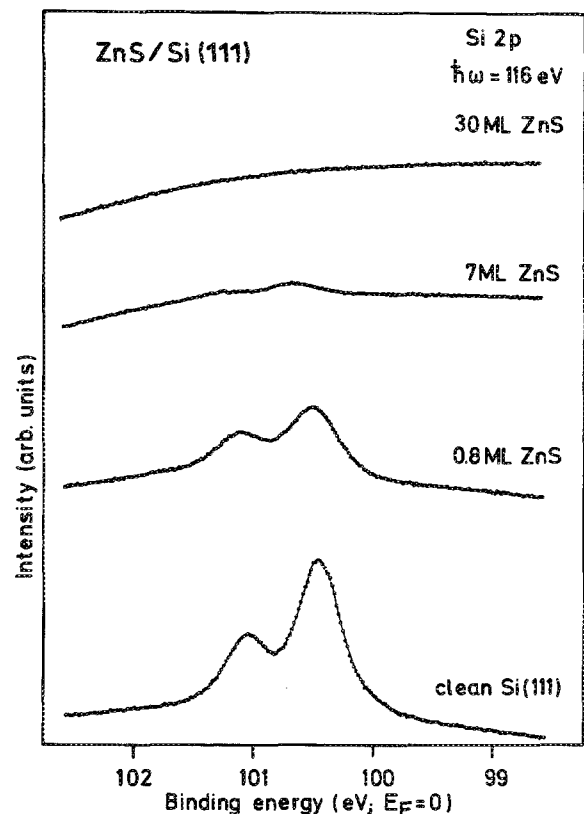


FIG. 4. Photoelectron spectra of the Si 2*p* level of the clean and covered Si (111)-(2×1) surface, recorded with a photon energy of 116 eV. The line shows the result of a curve fitting analysis.

$\chi_s = 2.5$), this shifted line most likely is related to a silicon-sulfur compound. Weser *et al.*,¹⁹ in their study of sulfur interaction with silicon, observed the formation of SiS_2 , which led to the appearance of a new core-level line shifted to higher binding energies by about the same amount. The more intense reaction between sulfur and $\text{Si}(111)-(7 \times 7)$ is reasonable if we consider the more open structure of this surface,²⁰ where the sulfur atoms find the Si adatoms which may be the sites where reaction most easily proceeds. Thus the $\text{Si}(111)-(2 \times 1)$ surface forms the more "ideal" substrate for a study of the heterojunction formation between ZnS and Si since the interface is more abrupt.

B. Determination of the valence-band offset

Studies of the valence-band offset using photoemission have been used extensively for an assessment of theories put forward for an explanation of the magnitude of ΔE_v , and lattice-matched systems like the one under consideration here are the most useful ones for this purpose. The valence-band-maximum (VBM) spectra, used in conjunction with band bending values derived from the Si $2p$ core level, provide a basis for the determination of ΔE_v ; they are shown in Fig. 5. These spectra were recorded at a photon energy of 58 eV, and the second-order light from the grating monochromator was used in order to excite the Si $2p$ level. The spectrum of the clean surface (bottom) exhibits a large density of states in the fundamental gap region of Si. This fact has been previously found and extensively studied by several authors.²¹ The usual procedure of determining the VBM from an extrapolation of the leading edge in the spectrum thus cannot be applied here. Since the location of the surface

states with respect to the valence-band edge is well known, however,²¹ their presence in the gap thus does not cause a major complication in our determination of the valence-band offset. Himpsel *et al.*²¹ observed that the surface states pinned the Fermi level at $E_F - E_{v,s} = 0.40$ eV for a flat cleaved surface, and at 0.46 eV for a cleave with many steps. For the annealed $\text{Si}(111)-(7 \times 7)$ surface they found a distribution of pinning positions centered around 0.63 eV. Himpsel *et al.* also showed that flat and stepped surfaces have different core- and valence-level line shapes. The flat cleaves possess a characteristic double surface state structure with a peak at $E_v - 0.6$ eV and a shoulder at E_v . The stepped surfaces, on the other hand, have a single smeared-out structure shifted towards lower binding energies. For flat cleaves the core-level spectra exhibit a considerably narrower distribution of surface core level emission than for stepped ones. This difference in behavior of "good" and "bad" cleaves was also found in our investigation.

In the valence-band spectra of Fig. 5, it is clearly seen that the surface state emission disappears upon deposition of ZnS which is consistent with the LEED patterns where the (2×1) reconstruction is lifted at such doses. The total width of the valence band decreases by about 0.4 eV, which is in agreement with the difference between E_F and $E_{v,s}$ of 0.40 eV.²¹ Upon further deposition of ZnS, the features of the valence band change quite remarkably. The spectrum at the highest coverage is quite similar to the one from a cleaved ZnS substrate²² indicating a well-ordered ZnS overlayer is present as far as can be told from the photoelectron spectra. We can exclude the existence of surface states in the gap of this semiconductor, not only from the theoretical treatment

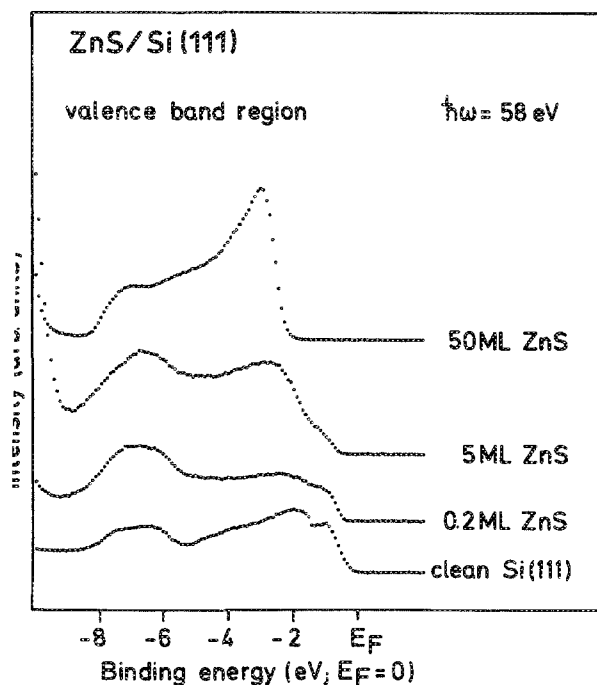


FIG. 5. Photoelectron spectra of the valence band of clean Si (111) (2×1) and that of different thicknesses of ZnS. The thick layer shows the emergence of clear peaks which are related to transitions from the ZnS valence band.

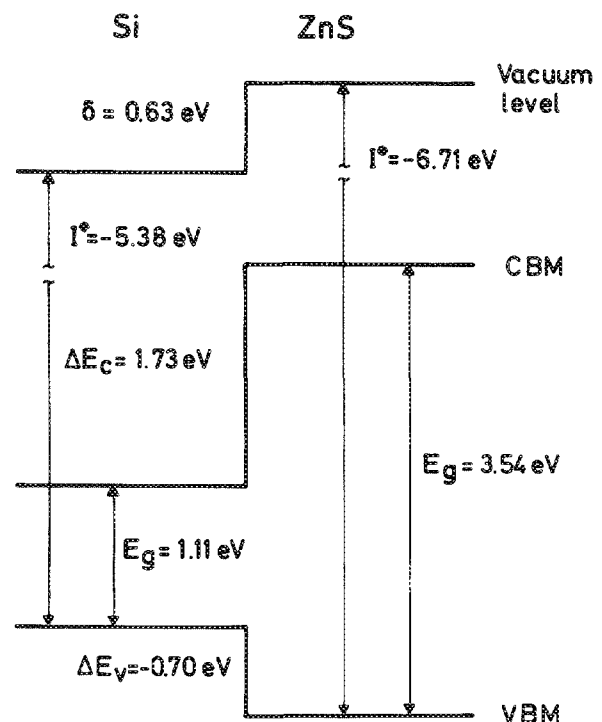


FIG. 6. Experimental values for the lineup of the valence bands, conduction bands, and vacuum level for ZnS/Si (111), based on the evaluation of ΔE_v , and the ionization energies I^* as well as the fundamental band-gap values.

of the structure of this surface,²³ but also from a comparison between our spectra and x-ray photoelectron spectra of the ZnS valence band,²² which show close agreement, despite the insensitivity of the XPS spectra to surface features. We are thus able to determine the valence-band maximum of the ZnS overlayer directly from the spectrum using the extrapolation mentioned above. Note in this context that this method is not fail-safe even for surfaces which exhibit no states in the gap; it has recently been shown^{24,25} that the top of the valence band in the angle-resolved spectra recorded at low photon energies is not properly described by the extrapolation of the edge, but by the correct determination of the direct transition of the topmost valence band at the Γ point of the bulk Brillouin zone. Since a careful determination of the distance between the leading edge of the spectra and this direct transition has not yet been carried out, we are left with the usual procedure, but have to keep in mind that a systematic error amounting to about 0.2–0.3 eV may be introduced in this way. The error is particularly large in the present case since in one of the samples, there is a correct way for the determination of E_v ; in studies of other systems which have a similar band structure at the VBM, as is the case for most III-V semiconductors, the error will largely cancel out.

The valence-band offset determined in the manner described above, for the ZnS/Si(111)-(2 \times 1) system, amounts to $\Delta E_v = (-0.7 \pm 0.2)$ eV. Here the error margin is much larger than in previous studies; this is not due to a specific problem in determining band bending or the VBM, but rather to a much larger scatter between different sets of data. The error margin for a single experiment is estimated, from the uncertainty in the core level binding energy and the VBM, to be about 0.05 eV. This is discussed in more detail below. Apart from the evaluation of ΔE_v , the photoemission technique also gives access to the work function change at the interface. From the total width of the spectrum and a precise knowledge of the photon energy, we can derive the ionization energy. For clean Si(111)-(2 \times 1), $I^* = 5.38$ eV, very similar to the value derived by Sebenne *et al.*²⁶ For the ZnS overlayer, $I^* = 6.7$ eV, considerably smaller than the value of Swank *et al.*,²⁷ measured on a freshly cleaved ZnS(110) surface; it is likely that the different crystal orientation [compared to our (111) direction] is the explanation for a large part of this difference. From the value for I^* , we derive a work function change of about 0.7 eV upon interface formation, which is shown in Fig. 6.

There are to our knowledge no previous reports of experimental band offset determinations for the ZnS/Si system. Among the approaches for obtaining predictions for band offsets, the semi-empirical table by Katnani and Margaritondo²⁸ has been widely used, which is based on room-temperature-deposited layers of Si and Ge onto a wide variety of semiconductor surfaces; unfortunately, ZnS was not studied by these authors. Even calculated band offsets are rare, despite the fact that this well-lattice-matched interface may serve as a model system. In Harrison's tight binding theory,²⁹ the VBM result from a superposition of the levels of the free cation and anion, combined with a universal interatomic coupling term which only contains the bond lengths. On the basis of the assumption that the interface dipoles are negli-

ble, the so-called "natural" line-up results in $\Delta E_v = -1.9$ eV.

Cardona and Christensen³⁰ have formulated their "Dielectric midgap energy" (DME) model in order to account at least partly for the dipole effects at the interface, even though the midgap energy or charge neutrality level (CNL), which eventually determines ΔE_v , is estimated from average bulk band structure data. They reach fair to good agreement with available experimental data for other systems; however, for the present case of ZnS/Si they predict $\Delta E_v = -1.7$ eV, i.e., a difference between theory and experiment of 1 eV. While the inclusion of the "real" valence-band maximum as discussed above might push our value for ΔE_v up to about 1.0 eV, a large disagreement still remains. One possible explanation for the good agreement between the DME values and the experimental results of Katnani and Margaritondo might be that their interfaces were all grown on nonpolar (110) zinc blende surfaces, while we compare DME values with our polar interfaces. Thus one might argue that the good agreement between the data of Katnani and Margaritondo and the DME model is in fact due largely to the absence of interface dipoles. This is consistent with observations by Margaritondo *et al.*³¹ who found that the accuracy of all linear models decreases when the data base is expanded from group IV and III-V semiconductors to II-VI compounds, i.e., to interfaces including strongly ionic materials.

In the case of an ideal planar (111) interface, an additional sheet of dipoles is introduced at the interface. Tersoff³² has considered this case in a thought experiment. He argues that embedding a sheet of dipoles δ_x in a semiconductor leads to a net screened dipole $\delta = \delta_x/\epsilon$, where ϵ is the static long-wavelength dielectric constant of the semiconductor. Since the screening charge in a semiconductor is confined to a region of a few Ångströms around the charge being screened, the extra valence-band discontinuity introduced by the sheet of dipoles corresponds to the screened dipole, which will thus change the balance between the CNLs. In the case of ZnS/Si(111), the dipole due to the polar interface decreases the valence-band offset down to a minimum value for an ideal planar geometry where the silicon and sulfur atoms form an abrupt interface, i.e., in the case of a ZnS(111)-A growth. This is the expected direction of change on the basis of our experimental data. The large electric fields existing between the two semiconductors may then induce migration of atoms across the interface, causing a reduction of the dipole. This process may explain the larger scatter in our data compared with previous investigations of ΔE_v between II-VI and III-V semiconductors, many of which were conducted on nonpolar cleaved zinc blende (110) surfaces. Again, an investigation of ΔE_v for ZnS/Si(100) will yield more information concerning this topic.

In conclusion, we have investigated the growth mode of ZnS layers deposited on Si(111) surfaces by molecular beam epitaxy. The initial deposition is characterized by an adsorbed sulfur layer, followed by ZnS(111) growth in the zinc blende modification. We have determined the valence-band offset, which is much smaller than expected on the basis of midgap energy level estimates.

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