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Photoelectron core-level spectroscopy and scanning-tunneling-microscopy study of the sulfur-treated GaAs(100) surface

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A study of the adsorption of sulfur on the GaAs(100) surface after *in situ* thermal desorption of a protective As capping layer is presented. The sulfur flux was generated by the decomposition of silver sulfide in an UHV-compatible electrochemical cell. Use of As-capped samples provided a means to study the interaction of sulfur with both the $c(2\times8)$ and (4×1) surface reconstructions. Scanning-tunneling-microscopy images of the sulfur-covered surface indicated the formation of disordered surface layers which display a diffuse (1×1) low-energy-electron-diffraction pattern. This (1×1) phase is attributed to the symmetry of the bulk structure visible through the disordered surface overlayer, caused by the adsorbed sulfur breaking the surface dimer bonds. Synchrotron-radiation core-level photoemission spectra indicate evidence of sulfur bonding to both gallium and arsenic at room temperature, but that the relative magnitude of these bonding interactions depends on the Ga/As ratio of the clean surface. Sulfur $2p$ photoemission spectra from the annealed surfaces show that sulfur diffuses into the topmost atomic layers as well as bonding to the surface. Annealing the sulfur-covered surface above 400 °C results in the formation of a (2×1) low-energy-electron-diffraction pattern with a dimer-row structure clearly visible in scanning-tunneling-microscopy images. Our results would suggest that the adsorption of sulfur on the $c(2\times8)$ clean surface results in dimer rows consisting of both arsenic and sulfur dimers, while only sulfur dimers are observed after adsorption on the (4×1) surface. The degree to which the clean surface band bending is altered on these respective surfaces appears to be related to the precise chemical composition of the dimer rows.

I. INTRODUCTION

Since Sandroff *et al.*[1] illustrated an increase in current gain of a heterojunction bipolar transistor from 30 to 2000 after spin coating a thin film of $Na_2S\cdot9H_2O$ onto the GaAs surface, aqueous sulfide treatments of this surface have attracted considerable attention. These treatments have been found to reduce the surface recombination rate,[2] enhance photoluminescence intensity,[3] and yield greater sensitivities of Schottky barrier heights to metal work functions.[4] There are several recent synchrotron-radiation photoemission spectroscopy (SR PES) reports[5–8] on the characterization of GaAs surfaces following chemical etches in aqueous sulfide solutions. It has been identified that after room-temperature (RT) treatment As-S, Ga-S, and S-S bonds are formed.[5] In a study of temperature-dependent changes on $(NH_4)_2S_x$-treated GaAs(100) surfaces, Scimeca *et al.*[6] have found that the intensity of the Ga-S component increases at the expense of the As-S intensity as the sample is annealed from RT. The predominance of Ga-S bonds after annealing in the 350 °C range had been previously observed on the same system by both Oigawa *et al.*[7] and Sugahara *et al.*[8] For these annealed surfaces, band bending was seen to be relaxed with a 0.3 eV shift of the Fermi level towards a flat-band condition. A reflection high-energy electron-diffraction (RHEED) and x-ray photoelectron spectroscopy (XPS) study of $(NH_4)_2S_x$-treated GaAs(100) surfaces[9] reported that, for RT adsorption, a (1×1) diffraction pattern was observed which changed to a (2×1) pattern after annealing in the 260–420 °C range. This latter phase was attributed to dimerized sulfur atoms adsorbed on Ga bridge sites. The (1×1) structure has been attributed by Ohno and Shiraisi,[10] using first-principles pseudopotential calculations, to S adsorbed on the bridge sites of either Ga- or As-terminated GaAs(100) surfaces.

Chemical treatments using *in situ* dry processes are inherently superior to wet chemical treatments in terms of surface contamination levels and homogeneity. However, relatively few studies of the *in situ* interaction of sulfur with the GaAs(100) surface have been reported. The adsorption of H_2S onto a GaAs(100)-$c(2\times8)$ surface at 425 °C, investigated by Massies, Dezaly, and Linh,[11] was

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found to change the surface reconstruction to a well-defined (2×1) phase, as determined using low-energy electron diffraction (LEED). The authors noted a dramatic decrease in the As (33 eV) Auger line intensity as a function of H_2S exposure while the Ga (55 eV) line remained constant. This change in both surface stoichiometry and surface structure was associated with an exchange reaction between S and As atoms in the surface layer. Tiedje *et al.*[12] have similarly suggested, from high-resolution photoemission data, that a treatment of the GaAs(100) surface with H_2S at RT followed by annealing at 400 °C passivates the surface through removal of As atoms and the formation of a GaS_x chemical species. Sugahara *et al.*[13] have studied the adsorption of sulfur (produced using an electrochemical sulfur cell) on wet-chemically-etched GaAs(100) surfaces, where the surface was sulfur exposed at elevated temperatures. SR PES spectra indicated that, similarly to the $(NH_4)_2S_x$-treated and annealed surface, Ga-S bonds were formed after oxide removal. Band bending for the n-type S-annealed samples was reduced by 0.2–0.3 eV.

In this paper we present the results of SR PES, scanning tunneling microscopy (STM), Auger electron spectroscopy (AES), and LEED studies of the interaction of sulfur with GaAs(100) reconstructed surfaces. The thermal "decapping" of As/GaAs(100) surfaces combined with an *in situ* sulfur flux from an electrochemical cell enabled a more systematic study of the surface modification induced by sulfur adsorption than is possible using wet chemical sulfide treatments. RT sulfur adsorption was found to lead to the formation of a disordered, chemically reacted surface layer through which the bulk (1×1) LEED pattern could be observed. Annealing above 400 °C resulted in the formation of a (2×1) LEED pattern with a dimer-row structure clearly observed in filled-state STM images. This (2×1) structure forms irrespective of the initial As concentration of the clean surface. Photoemission core-level spectra of this (2×1) surface lead us to conclude that, for the more As-rich $c(2\times8)$ surface, a complete exchange of As and S does not occur and the dimer rows consist of both As and S dimers. Adsorption on the (4×1) surface, however, results in the surface dimer rows consisting of exclusively sulfur atoms. In addition, we find a correlation between the dimer-row chemical composition and the magnitude of the Fermi-level movement towards a flatband condition.

II. EXPERIMENTAL

Soft XPS (SXPS) measurements using synchrotron radiation were performed on beam line 6.1 of the Synchrotron Radiation Source (SRS), Daresbury, U.K. The synchrotron radiation was monochromatized by a 1200 l/mm blazed grating and the energy distribution of the emitted photoelectrons measured using a hemispherical analyzer. The photon energy chosen for As and Ga 3d core-level analysis was 100 eV, providing maximum surface sensitivity with near-identical escape depths for the photoelectrons.[14] A photon energy of 190 eV was used to probe the S 2p core levels. Overall instrumental resolution at 100 eV photon energy was 0.3 eV. Photoelectron core-level spectra were curve fitted by assuming the Voigt profile—a Lorentzian convolved with a Gaussian line shape—using a nonlinear least-squares fitting routine, after subtraction of an appropriate background. The Gaussian broadening accounts for the instrumental resolution and also any broadening due to disorder and potential variations (nonhomogeneous band bending) across the surface. The Lorentzian shape is the natural broadening due to the finite lifetime of the core hole. The UHV tunneling microscope—in a separate UHV system in PTB, Braunschweig, Germany—was from Omicron Vakuumphysik GmBH and that vacuum vessel also contained a four-grid LEED/AES system.

The n-type (Si doped to $2\times10^{18}\text{cm}^{-3}$) As-capped GaAs(100) samples were indium bonded to a tantalum or molybdenum holder before introduction to either UHV system. They were decapped at 350 °C while the As pressure was monitored using mass spectrometry. After removal of the cap, annealing from 400–570 °C yielded the range of surface reconstructions previously reported.[15] Temperatures, in both systems, were measured using a Chromel-Alumel thermocouple mounted on the sample holder. The clean $c(2\times8)$ and (4×1) surfaces were subsequently exposed to a beam of molecular sulfur from a home-built electrochemical cell, as described previously.[16] The cell was operated at a current of 0.5 mA and surfaces were exposed to the sulfur flux for typically 5 min, yielding a saturation sulfur coverage, as determined from AES analysis.

III. RESULTS AND DISCUSSION

The core-level decomposition parameters used for the clean GaAs(100)-$c(2\times8)$ surface were within the range of previously reported values.[14,17–19] Figure 1 shows the results of the curve-fitting procedure applied to the As 3d spectrum for (i) the clean $c(2\times8)$ surface and (ii) the clean (4×1) surface. Three components in the fit were necessary to obtain the minimum χ^2 for the $c(2\times8)$ sur-

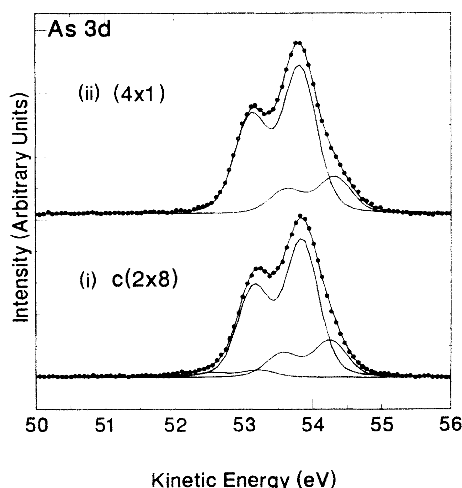

FIG. 1. As 3d core-level spectra measured on the decapped (i) $c(2\times8)$ and (ii) (4×1) GaAs(100) surfaces ($h\nu=100$ eV).

face. The core-level spectrum consists of the bulk As-Ga component and two surface core-level components shifted by 0.61 ± 0.02 and 0.40 ± 0.02 eV to higher and lower binding energy (BE), respectively. A number of previous studies[14,17,18] have identified the higher-BE component as being due to excess As atoms (remaining from the decapping procedure) bonded primarily to other As atoms. Further evidence that this is the case is visible in the As 3*d* spectrum of the (4×1) surface [Fig. 1(ii)]. At the higher annealing temperature needed to form this reconstruction, the excess As desorbs and the component at higher BE is absent from the spectrum. Ludeke, Chiang, and Eastman[20] identified the low-BE component with the As dimers terminating the $c(2\times8)$ surface. For the (4×1) surface, the lower-BE component shifts to 0.49 ± 0.02 eV, consistent with the results of Vitomirov *et al.*[18]

For the Ga 3*d* spectra in Fig. 2, three components are necessary in both cases to achieve a good fit of the experimental data. The two surface components in the $c(2\times8)$ spectrum are shifted by 0.42 ± 0.02 and -0.30 ± 0.02 eV relative binding energy. Ga also exhibited two surface components in the spectra of LeLay *et at.*[14] for the decapped $c(2\times8)$ surface which were not observed on the molecular-beam epitaxy (MBE) grown surface. However, the authors did not comment on the origin of the surface components. Two surface core-level shifted components are incompatible with a surface reconstruction consisting of only a three As dimer–one missing dimer unit cell for the $c(2\times8)$ surface, as was observed in the STM images of this surface presented by Pashley and Haberern.[21] For that unit cell, *all* Ga surface atoms are threefold coordinated and this should give rise to only one surface component in the core-level spectra. If the surface consists of (i) a two dimer–two missing dimer phase, or (ii) a mixture of both phases, the dimerization of underlying Ga as described by Farrell and Palmström[22] will give rise to another component. Interestingly, Vitomirov *et al.*[18] did not observe this second component in their studies of decapped GaAs(100) surfaces. This suggests that, in their case, the three As dimer–missing dimer unit cell was dominant across the surface.

For the (4×1) reconstructed surface [a disordered $c(8\times2)$ phase[20]], the magnitude of the surface component at lower relative binding energy in the Ga 3*d* spectrum increases with respect to that of the $c(2\times8)$ surface. This has also been observed in the data of LeLay *et al.*[14] That group identified the two surface components for the $c(8\times2)$ surface as being due to inequivalent dimers in the unit cell. They assumed the model of Frankel *et al.*,[23] where one dimer in which Ga is bounded to fourfold-coordinated As in the second layer is surrounded by two dimers in which Ga is bonded to threefold-coordinated second-layer As. Vitormirov *et al.*[18] observed that the relative binding energies and emission intensities of the surface shifted components are extremely sensitive to variations in the thermal desorption procedure and noted variations of as much as 0.1 eV in the binding energies from sample to sample.

A filled-state STM image of the (4×1) surface taken with a sample bias voltage of -2 V and a tunneling current of 1 nA is illustrated in Fig. 3. This image is qualitatively similar (albeit with poorer resolution) to very recent STM images of Skala *et al.*[24] of the $c(8\times2)$ surface; they proposed a model where uninterrupted rows of As dimers are separated by two rows containing Ga dimers. Their model directly implies a surface As concentration of 0.5 ML and is consistent with electron-counting heuristics, leading to no net surface charge imbalance. The authors cited both previous STM observations[25] showing that the most As-depleted $c(2\times8)$ reconstruction has a surface As concentration of 0.5, and a SR PES study[18] that determined that the intensity ratio *I*(As 3*d*):*I*(Ga 3*d*) for the $c(8\times2)$ reconstruction almost

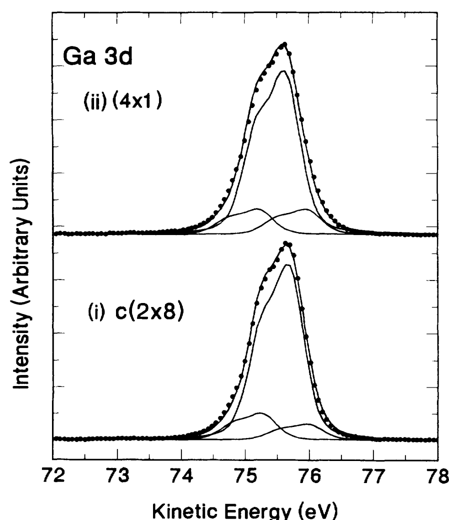

FIG. 2. Ga 3*d* core-level spectra measured on the decapped (i) $c(2\times8)$ and (ii) (4×1) GaAs(100) surfaces ($h\nu=100$ eV).

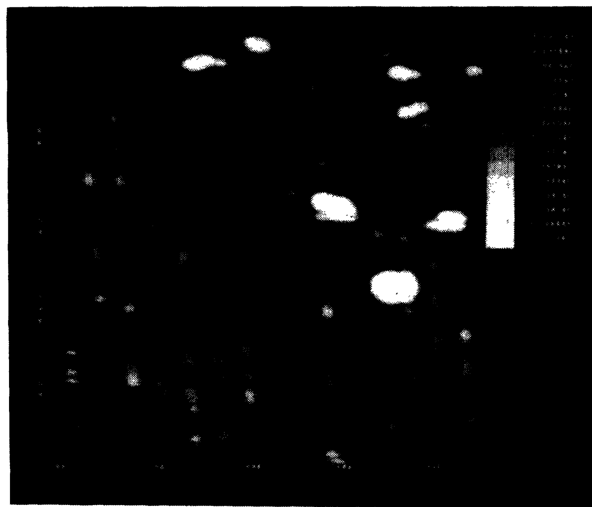

FIG. 3. Filled-state STM image of the GaAs(100-(4×1) surface ($V=-2$ V, $I_t=1$ NA). Nodes in the dimer rows are just resolved in a number of places.

equaled the lowest value obtained for the $c(2\times8)$ surface. Nodes in the dimer rows associated with the higher energy of the filled As lone-pair states relative to the As-As dimer bond, as also observed by Skala *et al.*,[24] are visible in areas in the image of Fig. 3.

One question regarding the photoemission data for the clean $(4\times1)/c(8\times2)$ surface remains to be answered. For the Ga 3*d* spectra, two surface components are required to achieve a good fit to the data in both our results and many other groups'.[14,17–19] If the model of the $c(8\times2)$ reconstruction proposed by Skala *et al.*[24] is correct, all surface Ga atoms are dimerized and thus in the same bonding configuration. Therefore only one surface component should be sufficient to fit the data. The reason for this discrepancy is at present unclear but may again be due to the existence of different unit cells across the surface. As the (4×1) phase is said to consist of disordered $c(8\times2)$ unit cells, this proposal may be plausible. A second explanation is in terms of the medium-energy ion-scattering (MEIS) data of Falta *et al.*[26] where intermixing of Ga and As in the uppermost atomic layer was proposed. Unfortunately, it is not possible to identify the exact origin of both Ga 3*d* surface components with our photoemission data while remaining consistent with the $c(8\times2)$ model of Skala *et al.*[24] which provides the best explanation of our STM data.

A clean $c(2\times8)$ surface was exposed to a sulfur flux from the electrochemical cell. The results of this exposure, with subsequent annealing at 250, 350, and 450 °C on both the As and Ga 3*d* core levels are displayed in Figs. 4 and 5, respectively. Room-temperature adsorption of sulfur [Fig. 4(i)] leads to the disappearance of the As 3*d* low-BE surface component, with two very broad components appearing at 1.1 and 1.7 eV higher relative BE. A smaller-magnitude broadened component exhibiting a chemical shift of 0.5 eV to higher binding energy

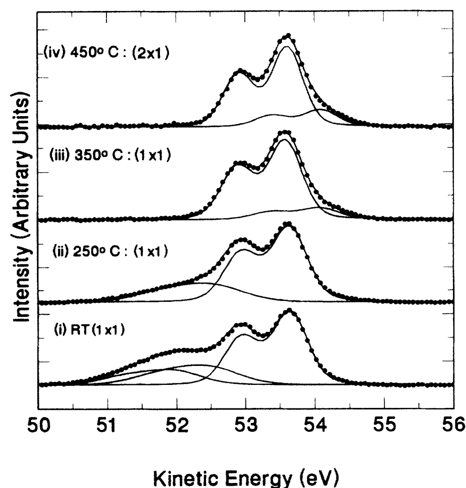

FIG. 4. Changes induced in the As 3*d* photoemission spectrum as a function of sulfur deposition and annealing ($h\nu=100$ eV).

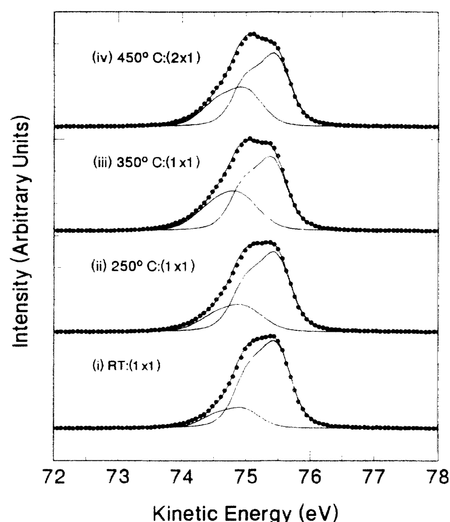

FIG. 5. Changes induced in the Ga 3*d* photoemission spectrum as a function of sulfur deposition and annealing ($h\nu=100$ eV).

appears in the Ga 3*d* spectrum [Fig. 5(i)]. For sulfur adsorption on the (4×1) surface this chemically shifted component was found to be greater in intensity than for the $c(2\times8)$ surface [increasing from 20% of the bulk component for the latter surface to 40% of the bulk component for the (4×1) surface]. The 0.5 eV chemical shift is in good agreement with the 0.55 eV value determined by Spindt *et al.*[27] for the $(NH_4)_2S$-treated surface. Like Spindt *et al.*,[27] we find no evidence of a second S-Ga component as was observed by Sugahara *et al.*[8] for $(NH_4)_2S_x$-treated surfaces. Both the etching rate and excess sulfur concentration of this latter solution were proposed as the origin of the second Ga-S bonding component. Further experiments by that group[13] using an electrochemical cell to expose chemically cleaned GaAs(100) samples to S at elevated temperatures have found only one Ga-S peak at 0.6 eV higher BE.

Although it is possible to fit the As 3*d* spectrum of Fig. 4(i) with a single, much higher-intensity broad peak due to sulfur, it was found that after annealing to 250 °C the component at +1.7 eV relative binding energy disappears while there is little change in the component at +1.1 eV. The component at +1.7 eV may be identified with As-S bond formation—the magnitude of the shift, however, is indicative of As sulfide compound formation. We attribute the component at +1.1 eV binding energy to remaining elemental As on the sulfur-treated GaAs(100) surface. The randomly bonded excess As remaining from the cap may react with the adsorbed sulfur forming a volatile arsenic sulfide compound that desorbs at relatively low temperatures. This would also explain the increase in intensity of the Ga-S component in the Ga 3*d* spectra of the (4×1) surface, as compared to the $c(2\times8)$ spectrum. A smaller elemental As surface concentration (coupled with a less As-rich surface reconstruction) will lead to a greater probability of Ga-S bond

formation. These surface chemical changes are accompanied by the disappearance of the $c(2\times8)$ surface reconstruction which is replaced by a (1×1) LEED pattern. This we attribute to adsorbed sulfur breaking surface As dimer bonds and the formation of a chemically reacted phase, particularly including As-S bond formation. The diffuse (1×1) LEED pattern originates from the underlying, unreconstructed GaAs.

While the As 3*d* chemically shifted component at 1.7 eV disappears after a 250 °C anneal [Fig. 4(ii)], there is an increase in the magnitude of the chemically shifted component in the Ga 3*d* spectrum. This removal of the 1.7 eV chemically shifted component in the As 3*d* spectrum was similarly observed by Spindt *et al.*[27] following annealing at 250 °C. The increasing dominance of Ga-S bonds over As-S bonds as the substrate temperature is raised has also been noted in a number of studies of aqueous-sulfide-treated GaAs surfaces.[6–8] This suggests a higher stability of Ga-S bonds over As-S bonds, which is to be expected considering their respective heats of formation and their relative bond energies as calculated by Ohno and Shiraishi.[10] After annealing at 350 °C [Figs. 4(iii) and 5(iii)], the 1.1 eV relative BE component in the As 3*d* spectrum is completely removed while there is a significant increase in the Ga-S intensity.

A considerable reduction in the diffuse background of the (1×1) LEED pattern occurs as the S-exposed GaAs(100) surface is annealed to 350 °C. From the As 3*d* core-level spectra in Fig. 4, it is evident that a single bulk component is insufficient to accurately fit the data. There is a reappearance of the lower-BE chemically shifted component which had disappeared following RT sulfur deposition. The presence of this component at this and higher annealing temperatures suggests that, throughout the annealing phase, there are always arsenic atoms present in the topmost atomic layer. Therefore for the sulfur-treated $c(2\times8)$ surface this (1×1) phase cannot be due solely to *S* bridge bonded to underlying Ga as has been reported by Lu and Graham[28] for the ammonium-sulfide-treated GaAs(100) surface. As suggested by Berkovits and Paget[29] the (1×1) pattern is most likely due to an amorphous sulfur layer which covers the surface, saturating dangling bonds and thereby preventing the formation of dimers. The (1×1) LEED pattern observed can therefore be attributed to the bulk-terminated GaAs pattern which is observed through a disordered surface layer.

Annealing above 400 °C results in the LEED pattern changing from a (1×1) to a (2×1) pattern. This sulfur-induced reconstruction was observed by Massies, Dezaly, and Linh[11] after H_2S treatment of the $c(2\times8)$ surface at 425 °C and has been more recently observed in both RHEED and other LEED (Ref. 30) studies. Massies, Dezaly, and Linh[11] suggested that for H_2S exposure at elevated temperatures, S exchanges with As in the topmost atomic layer, producing a (2×1) reconstruction. Estimates of the sulfur coverage by that group ranged from 0.7 to 1.0 ML, which supported their model. Again, from our spectra of the 450 °C–annealed surface, the presence of a surface core-level shifted component in the As 3*d* spectrum suggests that, for t'.e $c(2\times8)$ starting surface, a complete As-S exchange reaction has not occurred. In support of this argument, there is very little observable difference between the As 3*d* spectrum of the (2×1) reconstructed surface following the 450 °C anneal and that of the clean (4×1) surface which results after annealing at 570 °C. Further evidence that the (2×1) surface is terminated in both As-As and S-S dimers was provided by the reflectance anisotropy (RA) studies of Berkovits and Paget.[29] This group observed the appearance of a positive RA signal associated with the formation of S dimers after annealing an aqueous-sulfide-treated surface above 440 °C. The As dimer signal (of the same polarity) was, however, still present in the RA spectrum of the annealed surface. After complete desorption of S by annealing at 585 °C, both As and Ga dimer signals (with opposite polarity due to their orientation) were present in the RA spectrum.

The S 2*p* spectra for sulfur adsorption on the $c(2\times8)$ surface, shown in Fig. 6, clearly show two distinct chemically shifted components, separated by 0.5 eV, throughout the annealing sequence. (The photon energy was 190 eV; nonlinear least-squares fitting yielded a Lorentzian width of 0.21 eV, a spin-orbit splitting of 1.18 eV, and a branching ratio of 0.46.) These components cannot be attributed to Ga-S and As-S components, as above 250 °C there is no evidence of As-S bonding from As 3*d* spectra. The two components must therefore be related to S in two distinct bonding configurations bonded solely to Ga. We propose that the higher-BE component in Fig. 6 is caused by the indiffusion of sulfur into the top atomic layers of the sample, replacing bulk-coordinated As atoms. We argue that this component has higher BE than the sulfur bonded on the surface due to the fact that, when it becomes fourfold coordinate, it acts like a shallow donor and therefore appears at a higher BE than the surface-bonded sulfur. It is interesting to note that the BE of the $\frac{3}{2}$ component of this peak

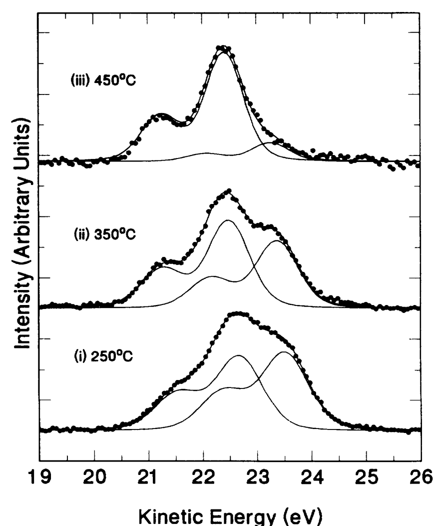

FIG. 6. S 2*p* photoemission spectrum as a function of annealing for the S/GaAs(100) surface ($h\nu = 190$ eV).

with respect to the valence-band maximum (VBM)—161.5 eV—is identical to that reported for bulk-coordinated sulfur atoms on the sulfur-annealed GaAs(111)A and (111)B surfaces.[31] The relative change in the intensities of these two S 2*p* components during the annealing cycles can be explained by the indiffusion of sulfur from the surface into the top atomic layers. An angle-resolved core-level study of the selenium-treated GaAs(100) surface by Maeda *et al.*[32] identified two distinct components in the Se 3*d* spectra, and they attributed the higher-BE component to bulk-coordinated Se atoms below the surface. The x-ray photoelectron diffraction study of Gallet and Hollinger[33] of the interaction of ammonium polysulfide with the InP(100) surface also indicated evidence of S-P exchange reactions extending a number of layers into the crystal.

The movement of the Fermi-level position following sulfur deposition and annealing is shown in Fig. 7. RT sulfur deposition results in a 0.2 eV shift towards the conduction-band minimum (CBM) from the clean-surface position of 0.85 eV above the valence-band maximum. This shift was determined by measuring the change in the binding energy of the bulk As 3*d* and Ga 3*d* components following sulfur deposition, referenced to a metallic Fermi level in contact with the sample. No change was detected in the Fermi-level position during the subsequent annealing until, at 570 °C, the sulfur desorbs from the surface and the clean-surface Fermi-level position is reestablished. This is accompanied by the appearance of the clean (4×1) LEED pattern and the disappearance of the S 2*p* photoemission and the S (152 eV) AES peak. Many previous studies of the interaction of aqueous sulfides with the GaAs(100) surface have noted a 0.2–0.3 eV Fermi-level shift towards the CBM (*n*-type sample) when compared with the untreated surface.[5,7,8] This shift only occurred after annealing in the 350–400 °C range and was attributed to the formation of Ga-S bonds.

As mentioned previously, a complete As-S exchange reaction would lead to the As 3*d* spectrum consisting of a single spin-orbit-split component as all the near-surface As would be bulk coordinated. This is the case for the Se-induced GaAs(100)-(2×1) reconstruction as reported by Takatani, Kikawa, and Nazakawa.[34] As for the sulfur-treated surfaces detailed in the present study, all Se-stabilized surfaces show a (2×1) reconstruction irrespective of the initial clean-surface reconstruction. The As 3*d* peak for the Se/GaAs(100-(2×1) surface was fitted with a single spin-orbit-split component. Similarly, for

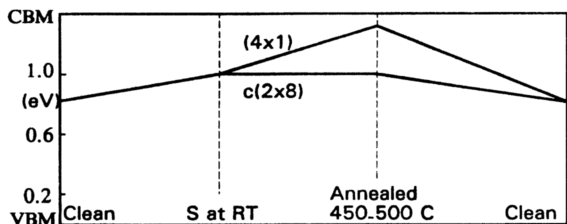

FIG. 7. Schematic illustration of the surface Fermi-level movements for sulfur deposition and annealing on the $c(2\times8)$ and (4×1) surfaces.

the sulfur-treated InP(100) surface, Gallet and Hollinger[33] found only a single phosphorus bulk-coordinated peak, while only the indium peak showed evidence of a sulfur-induced chemically shifted component.

RT deposition of sulfur onto the (4×1) surface reconstruction also led to the disappearance of the dimerized clean-surface reconstruction, which was replaced by a diffuse (1×1) LEED pattern. The STM image of the (4×1) reconstructed surface following RT sulfur adsorption, shown in Fig. 8(a), confirmed the presence of a disordered surface layer which persisted up to an annealing temperature of 400 °C. The subsequent chemical interactions of sulfur with the (4×1) surface were similar to those presented for the $c(2\times8)$ surface with two notable exceptions. First, the magnitude of the S-Ga chemically shifted component on the Ga 3*d* is larger for RT adsorption and increases in intensity as a function of annealing temperature. The magnitude of this component (80% of the bulk peak intensity at an annealing temperature of 450 °C) is such that it cannot be accounted for by a sulfur monolayer bonded on top of the surface.[35] Secondly, as can be seen in Fig. 9, it is possible to fit the As 3*d* peak with one single spin-orbit-split component following sulfur deposition and annealing to 500 °C where the surface exhibits a clear (2×1) LEED pattern. This suggests, in contrast to the results obtained on the sulfur-treated $c(2\times8)$ surface, that all the As near the surface is bulk coordinated and not involved in surface dimer formation. S 2*p* spectra of the annealed surface again displayed two distinct chemically shifted components consistent with surface- and bulk-bonded configurations.

Typical filled-state STM images of the S-induced (2×1) reconstruction formed on the (4×1) clean surface are shown in Fig. 8(b), taken with a sample bias of -2 V and a tunneling current of 1 nA. Attempts at imaging this surface at positive bias (i.e., empty-state imaging) were unsuccessful with considerable feedback loop instability. The dimer rows running in the [011] direction with an 8 Å period are clearly visible. It is interesting to note that it is not possible to resolve a node in any of the dimer rows, as was possible for the dimers on the clean (4×1) surface shown in Fig. 3. The filled-state charge density would therefore seem to be more spatially localized over the individual dimers. The relatively poorly ordered surface gives rise to a (2×1) LEED pattern with much broarder spots and higher diffuse background than that observed for the Se-treated GaAs(100) surface.[36] The Se-induced (2×1) reconstruction has been very recently shown by Biegelsen *et al.*[37] to consist of highly ordered dimer rows. As stated by that group, Se has a covalent radius closer to that of As than does S, leading to considerably less induced stress—and correspondingly, a higher degree of order—when Se exchanges with As.

A significant difference between the (2×1) surface formed on the (4×1) surface as opposed to the more As-rich $c(2\times8)$ surface is the degree of Fermi-level movement following a high-temperature anneal, also illustrated in Fig. 7. RT sulfur adsorption results in the Fermi level moving 0.2 eV towards the CBM as was observed for the sulfur-treated $c(2\times8)$ reconstructed surface.

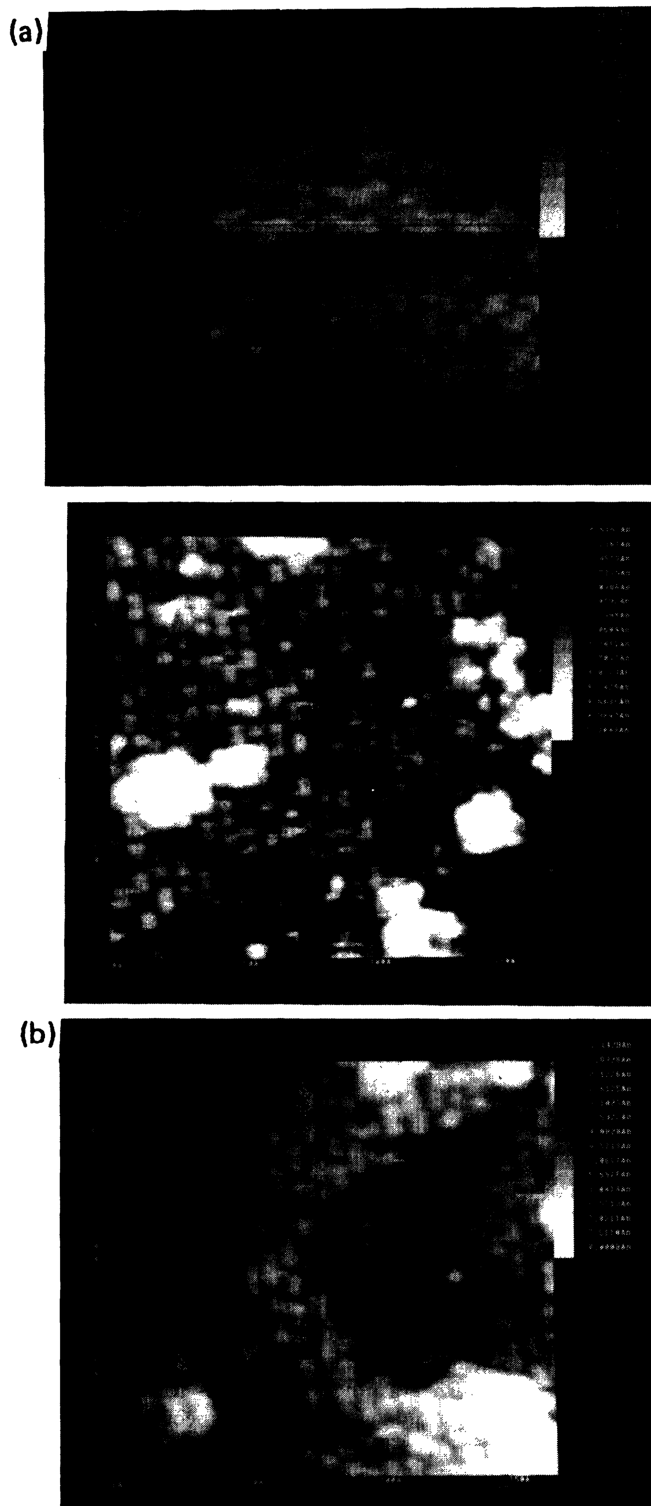

FIG. 8. (a) Filled-state STM image ($V=-2$ V, $I_t=1$ nA) of the amorphous overlayer observed after room-temperature sulfur adsorption on a GaAs(100)-(4×1) surface. Images of this nature persisted to annealing temperatures of 400 °C. (b) Typical filled- state STM images, taken with the same scan parameters as used for the clean GaAs(100)-(4×1) surface, illustrating the (2×1) dimer-row structure induced by sulfur adsorption and annealing above 400 °C. A bilayer step (2.8 Å) is visible in the lower image.

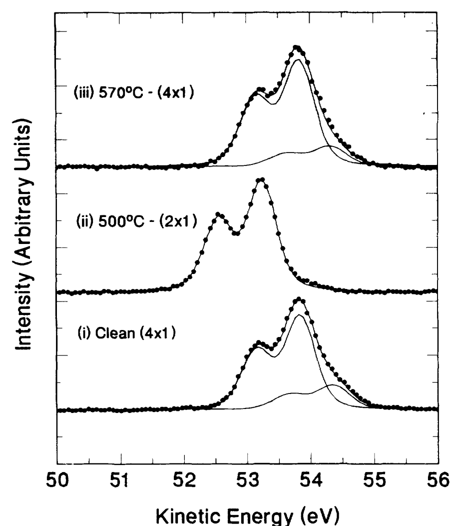

FIG. 9. As 3*d* core-level spectrum for (i) the clean GaAs(100)-(4×1) surface, (ii) after room-temperature sulfur adsorption and subsequent annealing to 500 °C, and (iii) after S desorption at 570 °C.

However, annealing at 500 °C results in a further movement of 0.3 eV towards the CBM. When the original position of the Fermi level is considered (0.85 eV above the VBM), this total movement of 0.5 eV corresponds to a Fermi-level position of 1.35 eV above the VBM, i.e., almost a flatband condition. Annealing the sulfur-treated surface again resulted in the desorption of the sulfur, the restoration of the clean-surface (4×1) LEED pattern, and a return of the Fermi level to its original clean-surface position.

Since the $c(2\times8)$ and (4×1) starting surfaces display the same LEED pattern following sulfur deposition and annealing, the conclusion from the photoemission studies is that the chemical composition of the dimer rows which result in the observation of a (2×1) LEED pattern must be variable. For this to be true we must assume that the As and S dimers have approximately the same scattering probability, as LEED does not distinguish between them. It appears that the chemical composition of the top atomic layer controls the degree of Fermi-level movement. For sulfur adsorption on the $c(2\times8)$ surface, the photoemission evidence would suggest that the (2×1) dimer rows are composed of both As and S dimers, while on the (4×1) surface these dimers are composed exclusively on sulfur atoms. This is in agreement with the results of Fermi-level movement reported by Scimeca *et al.*[38] for a study on the *in situ* adsorption of Se on the GaAs(100) surface. They reported that the maximum degree of Fermi-level movement was observed when all the surface As atoms had been replaced by Se atoms.

The reason why the total replacement of the surface As dimers with S dimers leads to a substantial flattening of the bands, or indeed why the sulfur atoms dimerize in the first place, is not clear. The calculations of Ohno and Shiraishi[10] suggested that, while dimerization may occur,

the energy gained in the process was very small. However, these calculations did not include the possible replacement of bulk-coordinated As atoms by S atoms in the topmost atomic layers which is evident from our studies. Since this indiffusion of sulfur into the surface is observed for both samples, it does not appear to be the critical factor in determining the different Fermi-level movements for the two starting surfaces. Possible geometries for the (2×1) sulfur-terminated GaAs(100) surface suggested by Ren and Chiang[39] are inconsistent with our results. Three of these geometries involved the bridging of As dimers with either a sulfur atom or sulfur dimer. As is evident from our core-level spectra, the (2×1) surface reconstructions that we observe involve only S-Ga bonding. From an electron-counting point of view, the neutral surface configuration would consist of equal numbers of As and S dimers, or alternatively As-S dimer formation as proposed by Chadi,[40] While the former possibility may be achieved on the sulfur-treated $c(2\times8)$ surface, it obviously does not lead to maximum Fermi-level movement. There is no evidence from the photoemission studies of any As-S dimer formation, as may occur for GaAs(100)-(2×1):Se.[37] A further possibility would be a surface consisting of S dimers and vacancies. From the STM images of Fig. 8(b) it is evident that, while vacancies are present—suggesting that surface charge neutrality is indeed most likely obtained via the removal of S dimers—an ordered array of missing dimers [as observed for the clean GaAs(100)-$c(2\times8)$ surface] does not occur.

The different surface chemistries are obviously related to the chemical compositions of the two clean starting surfaces. The higher content of surface As on the $c(2\times8)$ surface leads to a larger As-S interaction. When this surface is heated, the arsenic sulfide desorbs, removing sulfur from the surface. On further annealing this surface, As and S dimers form, although this does not result in any further reduction in band bending. On the (4×1) surface, there is less surface As present and this results in less As-S compound formation during the annealing phase and correspondingly more Ga-S bond formation. The critical factor in determining the extent of the Fermi-level movement therefore appears to be the As content of the top atomic layer.

The question which must be addressed is whether the Fermi-level movements towards the CBM are indicative of an unpinning or simply a repinning of the Fermi level. From electron-counting rules, a dimerized sulfur-terminated GaAs(100) surface with sulfur also replacing As atoms below the surface is not neutrally charged. The calculations of Ren and Chiang[39] for the formation of sulfur dimers on the GaAs(100) surface showed that a S-S antibonding state would have an energy which would make it coincident with the bulk CBM. What may well be occurring is that the sulfur dimers result in a reduction of the midgap surface states responsible for band bending on the clean (4×1) surface reconstruction, while introducing antibonding states close to the CBM. Only when the midgap surface density has been totally eliminated by the termination of the surface in exclusively sulfur dimers will the Fermi level move close to the CBM. This condition is only fulfilled on the (4×1) surface due to the nature of the surface chemistry. From our studies to date, it is impossible to distinguish between an unpinning of the Fermi level resulting in its movement towards the CBM and a repinning as described above, which would result in similar Fermi-level movement. What we can nevertheless state is that the degree of band flattening observed for sulfur deposition and annealing on the (4×1) surface will significantly reduce the surface recombination rate and enhance the photoluminescence intensity. This does not necessarily mean that the magnitude of the Schottky barriers formed on this surface will reflect variations in the work functions of the metals deposited.

IV. CONCLUSIONS

In summary, the room-temperature adsorption of sulfur on either the $c(2\times8)$ or (4×1) GaAs(100) surfaces leads to a removal of the dimerized reconstructions with the appearance of a (1×1) LEED pattern. This pattern is due to the unreconstructed bulk GaAs structure showing through a disordered, chemically reacted surface layer. On annealing above 400 °C, the (1×1) pattern is replaced by a (2×1) pattern which corresponds to a dimer-row structure. Core-level photoemission spectra suggest that, for adsorption on the clean $c(2\times8)$ surface, the dimer rows consist of As and S dimers, while for the sulfur-treated (4×1) surface they are formed solely by S atoms. The composition of these dimer rows has a strong influence on the changes in the surface Fermi-level position. These findings for the (4×1) surface are very similar to those reported for the selenium-treated GaAs(100) surface at elevated temperatures. Finally, the fact that it is possible to obtain almost flatband conditions on the sulfur-treated GaAs(100) surface by following the correct surface preparation procedure is significant for the potential technological applications of this surface.

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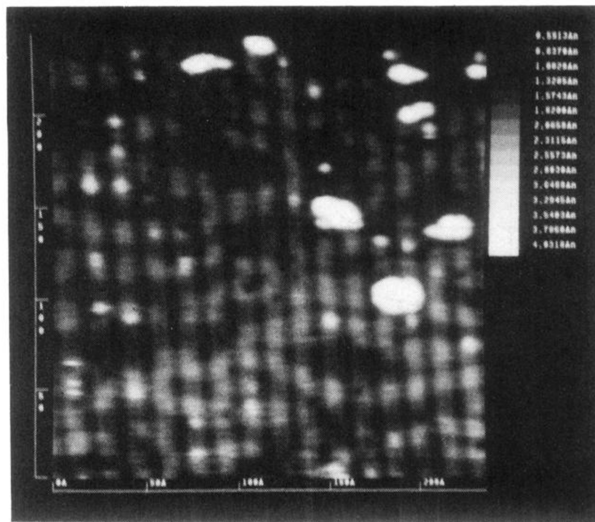

FIG. 3. Filled-state STM image of the GaAs(100-(4×1) surface ($V=-2$ V, $I_t=1$ NA). Nodes in the dimer rows are just resolved in a number of places.

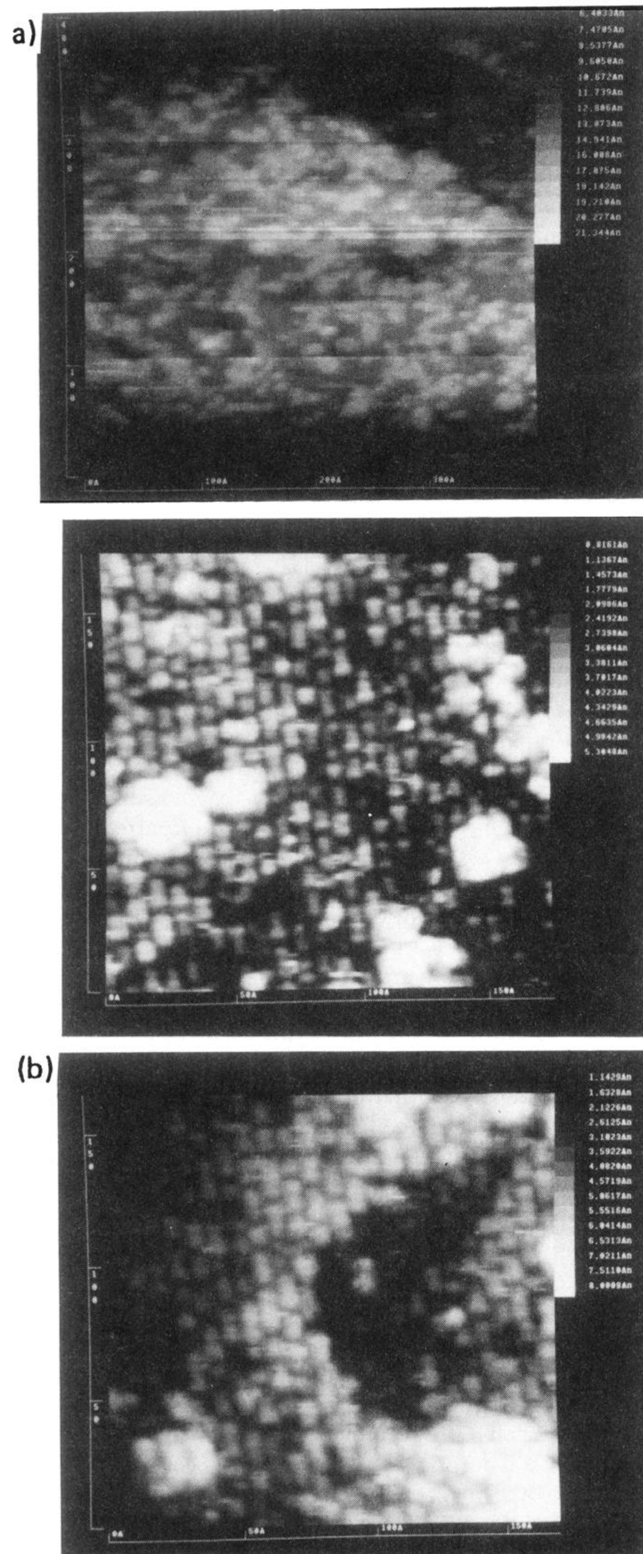

FIG. 8. (a) Filled-state STM image ($V = -2$ V, $I_t = 1$ nA) of the amorphous overlayer observed after room-temperature sulfur adsorption on a GaAs(100)-(4×1) surface. Images of this nature persisted to annealing temperatures of 400 °C. (b) Typical filled- state STM images, taken with the same scan parameters as used for the clean GaAs(100)-(4×1) surface, illustrating the (2×1) dimer-row structure induced by sulfur adsorption and annealing above 400 °C. A bilayer step (2.8 Å) is visible in the lower image.