Sulfide-passivated GaAs(001). I. Chemistry analysis by photoemission and reflectance anisotropy spectroscopies

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We have investigated the surface chemistry of $(NH_4)_2S$ -passivated GaAs(001) by studying this surface after passivation and after several subsequent annealings. We have used ultraviolet photoemission spectroscopy (UPS) at a near-normal takeoff angle and at a takeoff angle of 70°. We have also used, in the same ultrahighvacuum chamber, reflectance anisotropy spectroscopy, which probes the optical transitions due to surface dimers, and therefore provides useful information for the interpretation of core-level spectra. We find that gallium dimers appear after annealing to 520 °C due to sulfur desorption. At the same stage, there appears in the corresponding 3*d* core-level spectrum a surface component lying at a relative binding energy of -0.32 eV with respect to the volume contribution. Arsenic dimers appear after annealing to 360 °C, following the desorption of excess arsenic. In the same way, there appears in the arsenic 3*d* core-level spectrum a component at a relative binding energy of -0.28 eV. After desorption of the passivating overlayer the gallium-terminated part of the surface is essentially covered with sulfur. These sulfur atoms are dimerized, and contribute to a line in the reflectance anisotropy spectrum. At this same stage, the arsenic-terminated one is covered with excess arsenic. Unlike what was believed previously from UPS analysis, As-S chemical bonds are situated only in the passivating overlayer, which contains no gallium atoms. Comparison of the core-level spectra as a function of takeoff angle shows that the progressive desorption of this overlayer produces a change of its morphology.

I. INTRODUCTION

To study optical transitions on clean semiconductor surfaces, reflectance anisotropy spectroscopy (RAS) was developed a few years ago.^{1,2} RAS is based on the low symmetry of the surface of cubic semiconductors and consists of measuring as a function of light energy the relative difference in reflectivity for directions of the incident-light polarization along two orthogonal axes of the surface. In the particular case of GaAs(001), anisotropy arises due to formation of the arsenic and gallium surface dimers with the axes oriented along [110] and [110], respectively.^{2,3} The dimer optical transitions are dependent on light polarization as for diatomic molecules and therefore are polarized along the dimer direction. Their known RA signature consists of a line, at an energy which characterizes an internal transition of the dimer, with a conventionally positive sign for the $[1\overline{10}]$ direction, that is, for arsenic dimers, and a negative sign for the [110] direction, that is, for gallium dimers.² In a previous work,⁴ we have shown that RAS can be applied to analyze surface chemical bonds: after annealing to a given temperature, the breaking of these bonds induces the formation of additional dimers, which are revealed from a corresponding change of the RA spectrum. This was shown directly in the case of residual impurity desorption by comparing RA results with Auger results.⁵

The use of this technique together with the more conventional ultraviolet photoemission spectroscopy (UPS) allows a deeper understanding of surface chemistry, for two main reasons. First, it provides an independent information on the chemistry, which is useful for the deconvolution of corelevel spectra. The surface dimers found by RAS are believed to give rise to a distinct surface component in the core-level spectra, because the atoms involved in these dimers do not have the same charge state as the other atoms. The relative binding energies of the surface components due to dimers in As 3d and Ga 3d core-level spectra will be discussed elsewhere.⁶ Second, RA spectroscopy only probes chemical bonds situated on the semiconductor surface, and not in an amorphous overlayer that covers it.⁴ Thus, comparison of the data obtained using the two techniques allows us to determine the localization of these chemical bonds.

The aim of the present work is to apply this approach to the study of the surface chemical properties of GaAs(001)

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passivated by sulfide-containing solutions. This passivation has appeared as a potentially attractive method for reducing the surface recombination velocity,⁷ and for covering the sample with a protective overlayer.⁸ Sulfide-passivated surfaces have been studied, mainly in the case of $(NH_4)_2S_x$ passivation (x>1), but also in the case of $(NH_4)_2S$ and Na₂S passivations.⁹ We consider here, as a model system, the case of ammonium-sulfide-passivated GaAs. In a distinct work,¹⁰ we correlate this chemical information with the electronic properties of the same sulfide-passivated surface.

After passivation and introduction into the ultrahighvacuum (UHV) chamber, the as-treated surface is covered with an amorphous protective overlayer consisting mainly of sulfur.⁹ Since the interface between the passivating overlayer and the semiconductor surface has been found to be abrupt,⁸ it is possible to distinguish between the atoms situated in the passivating overlayer and the first layer of atoms which are bonded the semiconductor surface. Infrared (IR) absorption experiments demonstrate that the overlayer also contains arsenic, whereas no gallium is observable.¹¹ UPS studies reveal from the analysis of arsenic and gallium core-level spectra the existence of Ga-S and As-S bonds.¹² Annealing experiments show that As-S chemical bonds are broken at a relatively low temperature, approximately 200 °C, whereas desorption of sulfur from the surface, through breaking of Ga-S bonds, occurs above 500 °C.^{8,12,13}

In our previous work^{4,5} we find that these surfaces exhibit three main sulfur-related annealing stages: (i) Desorption of the passivating residual overlayer, revealed by the dimerization of sulfur atoms bonded to gallium, which produces the appearance of a positive line in the RA spectrum. (ii) Appearance of arsenic dimers, at least in the case of the Na₂S-passivated surface, after annealing at 400 °C. It is tempting to conclude that this appearance is due to breaking of As-S chemical bonds. However, the annealing temperature is much higher than the one at which photoemission spectroscopy shows the disappearance of As-S bonds.^{9,12,13} (iii) Breaking of Ga-S bonds, which results in the appearance of the characteristic gallium dimer signal.

II. PRINCIPLES AND EXPERIMENT

The principles of RAS study of sulfide passivation of GaAs(001) surfaces have been exposed elsewhere.^{4,5} RA spectroscopy consists in measuring, as a function of photon energy, the quantity given by

$$\frac{\Delta R}{R} = \frac{R_{[1\bar{1}0]} - R_{[110]}}{R},\tag{1}$$

where $R_{[110]}$ and $R_{[1\bar{1}0]}$ are the reflectances for incident light polarized along the two corresponding axes of the (001) surface. There are quite generally three possible contributions to a given spectrum: (i) A broad background, which can be attributed to the presence of a macroscopic anisotropy of the surface or of the film which covers this surface.¹⁴ The intensity of this background depends on the semiconductor dielectric function so that, in our case, the signal decreases with decreasing energy in most of the spectral range. (ii) A derivativelike structure appearing at energies corresponding to the E_1 and $E_1+\Delta_1$ bulk transitions, that is, near 3 eV, due to the linear electro-optic effect.¹⁵ This signal is mostly observed in doped materials because its intensity is proportional to the surface electric field. (iii) The anisotropic signals due to optical transitions related to the surface dimers. These signals are a negative signal at 2.2 eV for gallium dimers, and positive signals at a respective energy of 2.5 eV for sulfur dimers, and 2.9 eV for arsenic dimers. Note that the last signal is situated at an energy similar to the one of the signal due to the linear electro-optic effect. However, these two contributions can generally be separated because the shape of the dimer line, which is a well-defined Gaussian line of half width of the order of 0.3 eV, is very different from the derivativelike shape of the signal induced by the surface electric field.

The experiment was performed at the SU6 undulator beam line of the SuperAco storage ring of Laboratoire pour l'Utilisation du Rayonnement Electromagnetique (LURE), using the PES 2 station. Keeping the incident photon energy constant (100 eV), the photoelectrons were collected at normal emission and at an angle of 70° in order to increase the surface sensitivity. Their energies were analyzed by an angleresolved hemispherical electrostatic analyzer, whose angular acceptance is 2° . The overall energy resolution was below 250 meV. Samples were Joule heated, the temperature being controlled by an IR pyrometer.

For the RAS *in situ* investigations, we have transported the optical setup that we used for our previous RAS studies of sulfide-passivated GaAs from Ecole Polytechnique to LURE,^{4,5} and we have aligned it with the UHV chamber. This setup is closely analogous to the one built in St. Petersburg described elsewhere.¹⁶ The glass window of the UHV chamber, although not specially designed for RAS, was carefully selected among different windows in order to minimize parasitic effects in the spectrum due to birefringence.

The sample is a *p*-type GaAs epitaxial layer of acceptor concentration in the 10^{16} cm⁻³ range, grown at Laboratoire Central de Recherches, Thomson CSF. This sample is misoriented by approximately 2° towards the (110) orientation. It was dipped for 5 min into a fresh 0.75*M* solution of (NH₄)₂S at 60 °C, and subsequently underwent a rapid deionized-water rinsing and an isopropanol rinsing, after which the sample was immediately put into the introduction lock under a flow of nitrogen gas. Care was taken to minimize the sample exposure to light and ambiant air. In order to avoid spurious oxidation of the sample surface by excited oxygen, the pressure gauge in the introduction lock was switched off. Afterwards, the chamber working pressure remained better than 3×10^{-10} mbar.

The principle of the experiment is to perform successive annealings of the sample at increasing temperatures, in order to progressively desorb the passivating overlayer and to reveal a clean GaAs(001) surface. After each annealing, and cooling to room temperature, we investigate the modifications of both RAS spectra and UPS core-level spectra, and of the valence-band spectrum as well. We have performed several distinct annealing steps, of approximately 20 min. The temperatures, calibrated in a separate experiment, are, respectively, 150, 250, 270, 360, and 520 °C.

III. RESULTS

A. RAS results

The RA spectra of the surface after the various annealing stages are shown in Fig. 1. The spectrum of the as-treated



FIG. 1. RA spectra taken at room temperature after annealing at a temperature indicated between parentheses. Curve (b) shows the spectrum of an oxidized sample. The other curves were taken using a $(NH_4)_2S$ -passivated sample after successive annealings to temperatures indicated between parentheses. Curve (c) is the difference between the RA spectrum after annealing to 270 °C and the one of the as-treated surface.

surface, shown in curve 1(a), consists of a broad signal which depends weakly on energy, and covers the whole spectrum. Superimposed on this signal is a derivativelike structure, in the 2.8-3.2 eV region.

As found from the discussion of the preceding section, the broad signal is essentially due to macroscopic anisotropy whereas the derivativelike structure is caused by the linear electro-optic effect. In order to determine the possible contribution of dimers to the RA signal, we have taken, in the same experimental setup, the RA spectrum of a naturally oxidized piece of the same p-type wafer. This spectrum, shown in curve 1(b), is closely analogous to the above spectrum. For this oxidized surface the dimer signal is either absent of very small. Indeed we have found independently, in a case where no broad background signal is present, that the oxygen desorption from the surface coincides with the appearance of dimer signals, because surface oxygen saturates surface dangling bonds and prevents the formation of dimers.^{4,5} Thus we conclude that, on the as-treated surface, the dimer signal is, in the same way, very small and that the broad signal is almost entirely due to macroscopic anisotropy of the layer which covers the surface. This anisotropy is probably induced by an array of steps oriented along the [110] direction which, as shown by scanning tunneling microscopy (STM),¹⁷ is caused by the slight misorientation of the surface away from the (001) direction. Note that the decrease of the signal that we found after annealing is expected not to affect its spectral dependence but only its intensity, since this spectral dependence is essentially determined by the substrate dielectric constant.¹¹



FIG. 2. Decomposition of the RA spectrum after annealing at 360 °C, which shows the presence of arsenic dimers [curve (a)] and sulfur dimers [curve (b)]. Curve (c) is the background signal as found from the RA spectrum of the as-treated surface [curve 1(a)]. Curve (d) is the sum of curves (a), (b), and (c), and lies close to the experimental data (solid line).

The evolution of the RA spectra after annealing is very similar to the one found in previous works.^{4,5} Shown in curve 1(c) is the difference between the spectrum of the astreated surface and the one after annealing at 270 °C. This spectrum reveals the characteristic line at 2.5 eV, of width 0.35 eV, earlier identified as due to optical transitions in sulfur dimers on the Ga-terminated part of the surface.⁴ These dimers appear on the semiconductor surface after desorption of the amorphous passivation overlayer, which leaves a sulfur layer of the order of one monolayer on the semiconductor surface. Also present in this spectrum is a derivativelike structure between 2.8 and 3.2 eV, which reflects a change of the surface barrier.

Annealing at 360 °C leads to a decrease of the broad background. As can be seen by comparing curve 1(d) with the RA spectrum of the as-treated surface, reproduced in curve 1(e), this decrease is visible in the UV region above 3.5 eV, where no surface optical transition occurs. On the other hand, an increase of the RA signal near 3 eV reveals the appearance of dimer-related optical transitions. We can subtract the background signal because it has the same line shape as in the RA spectrum of the as-treated surface. This is shown in Fig. 2, where this background has been attenuated by a factor of 0.7 in order to fit the RA spectrum above 3.5 eV [curve 2(c)]. The remaining spectrum can be decomposed into two relatively narrow Gaussian lines. The corresponding RA signals are the above sulfur dimer line at 2.5 eV [curve 2(b) and the arsenic dimer line at 2.9 eV [curve 2(a)]. These two lines have the same positions, the same widths, and approximately the same magnitudes as in a previous work.⁴ The final agreement between the experimental data and the sum of curves 2(a)-2(c), shown in curve 2(d), is very good, except near 3 eV due to the linear electro-optic effect. We conclude that annealing at 360 °C produces the breaking of arsenic-related surface bonds and gives rise to the appearance of the arsenic dimers on the surface.

The RA spectrum after annealing at 520 °C, shown in curve 1(f), exhibits an intense negative line at 2.2 eV, due to



FIG. 3. Valence-band photoemission spectra under excitation by a 100-eV photon beam, taken at room temperature after annealing to the indicated temperature. Curve (e), obtained by difference, exhibits the Ga-S-related level in the valence band.

gallium dimers, induced by the desorption of sulfur and by the breaking of Ga-S chemical bonds. This has been verified in an independent work on the same sample, using Auger spectroscopy to monitor the decrease of sulfur concentration on the surface.¹⁰ Note that this annealing produces a modification of the arsenic dimer line, which has been observed before.⁵ The background signal completely disappears, which indicates that its origin is related to the monolayer of atoms covering the surface after the final anneal.

B. Valence-band spectra

The modifications of the valence-band spectra, shown in Fig. 3, are in agreement with the picture derived from the RAS analysis. The spectrum after annealing at 520 °C, shown in curve 3(d), is close to the one of the clean surface.¹⁸ On the other hand, the valence-band spectrum after the annealing stage at 360 °C contains, together with the features characteristic of the clean surface, an additional strong peak situated roughly 2 eV below the valence-band maximum. This can be seen in more detail in curve 3(e), which shows the difference between the spectra after annealing at 360 and 520 °C. This peak cannot be due to Ga-O bonds, for which the contribution to the valence-band spectrum would be different.¹⁸ A similar signal has been observed previously on sulfur-passivated surfaces.¹⁹ This signal is very likely due to states introduced by the Ga-S chemical bonds, because all As-related bonds have been broken by the preceding annealing stages. Note that there is an additional very broad signal at a lower energy. This component is at least partly due to the secondary electron emission produced by modification of the surface.

With respect to the above spectra, the valence-band spectra corresponding to the preceding annealing stages [curves 3(a) and 3(b)] are perturbed, because of the presence of

arsenic-related surface bonds. Breaking of these bonds together with desorption of the passivating layer can be followed by the progressive appearance of the spectrum discussed above.

C. Core-level spectra

In order to obtain a reliable decomposition of the corelevel spectra and to have more information on the geometry of the system, we have used a takeoff angle of 0° and also of 70°, which enhances the surface contribution. The corresponding arsenic 3*d* core-level spectra are shown, respectively, in Figs. 4 and 5, and the gallium 3*d* core-level spectra are shown in Figs. 6 and 7. The surface contributions to these spectra will be symbolized under the form A_i for arsenic and C_i for gallium.

Qualitative analysis of the gallium core-level spectra supports the picture derived by RAS: at both takeoff angles, the spectra after annealing to 150 and 250 °C, not shown in the figures, are identical to the ones of the as-treated surface. After annealing to 270 and 360 °C, the changes in these spectra are very small. This indicates that no Ga-related chemical bonds on the surface are broken by these low-temperature annealings. On the other hand, the change in this spectrum produced by annealing at 520 °C is strong. This is related to the disappearance of Ga-S chemical bonds and to the appearance of gallium dimers, already discussed above.

A deconvolution of the As 3d core-level spectra allows us to isolate several surface components. As can be seen in Fig. 4, the As 3d core-level spectrum at zero takeoff angle exhibits a broad component at a larger binding energy, which disappears after annealing at 270 °C. This observation is in agreement with previously published results,²⁰ which assign such a component to As-S chemical bonds. This component disappears after the annealing stage, which corresponds to the total desorption of the passivating overlayer. This shows that, as already proposed in Ref. 8, the As-S bonds are located in the passivating overlayer and not on the semiconductor surface, which is confirmed by the fact that this broad component is stronger at a takeoff angle of 70°.

As seen in Fig. 8, comparison between the As 3d corelevel spectra of the as-treated surface [curve 8(a)] and the one after the final annealing stage at 520 °C [curve 8(b)] shows that there also appears a component at lower binding energy. This evolution is related to the appearance of As dimers. Curve 8(c) shows the difference between the As 3dcore-level spectrum after passivation [curve 8(a)] and after annealing to 520 °C [curve 8(b)]. This curve shows a broad negative signal, which we label A_2 , at a higher binding energy, due to the disappearance of As-S chemical bonds. At a lower binding energy lies the contribution which appears after annealing. This contribution lies between 54 and 55 eV, and exhibits the spin-orbit structure. It can be seen that this shape is asymmetric, so that its interpretation requires the use of two distinct components, which we label A_4 and A_5 . Curve 8(c) shows an additional component in the intermediate energy range between 53 and 54 eV. This contribution can be isolated by taking the difference, shown in curve 8(d), between the spectrum of the as-treated surface and the spec-





FIG. 4. As 3d core-level spectra at 0° takeoff angle, as a function of annealing temperature. For the deconvolutions, the bulk contribution is shown by a dashed line. The sum of the fitted components is barely visible, as it perfectly fits the experimental signal.

FIG. 5. As 3d core-level spectra at 70° takeoff angle, as a function of annealing temperature.



FIG. 6. Same as Fig. 4, but for Ga 3d.



The same analysis can be performed for the gallium core-



FIG. 7. Same as Fig. 5, but for Ga 3d.

level spectra, as shown in Fig. 9, which compares the corelevel spectra after annealing to $360 \,^{\circ}\text{C}$ [curve 9(a)] and $520 \,^{\circ}\text{C}$ [curve 9(b)]. The difference between these spectra [curve 9(c)] shows the disappearance of a component at a kinetic energy of 75.5 eV together with the appearance of a



FIG. 8. Extraction of surface components of the As 3d corelevel spectrum at a takeoff angle of 0° by taking differences. Curves (a) and (b) are the spectra of the as-treated surface and after annealing to 520 °C, with their difference shown in curve (c). Curve (d) is the difference between the spectra after annealing to 150 °C and of the as-treated surface. Also shown are the components A_3 , A_4 , and A_5 obtained from the deconvolutions, which are very similar to the structures shown in curves (c) and (d).

contribution at an energy of 76.4 eV. In the following, these two components will be labeled C_3 and C_5 .

IV. ANALYSIS OF CORE-LEVEL SPECTRA

A. Deconvolution method

As shown before (Figs. 8 and 9), some of the surface contributions can be isolated by taking differences between



FIG. 9. Same as Fig. 8 for the Ga 3*d* spectra. Curves (a) and (b) are the spectra after annealing to, respectively, 360 and 520 °C, with their difference shown in curve (c). This difference shows that a component at a binding energy of 75.4 eV has disappeared. This component, labeled C_3 , is due to Ga-S chemical bonds. Conversely, there appears a component, labeled C_5 , due to gallium dimers. Also shown are the shapes of components obtained from the deconvolutions.

TABLE I. Parameters used for the deconvolution of all components, except as shown in Table II, A_2 and C_1 , of the As 3*d* and Ga 3*d* core-level spectra.

	As 3d	Ga 3 <i>d</i>	
Spin orbit (eV)	0.68	0.432	
Branching ratio	1.42	1.47	
Gaussian width (eV)	0.38	0.38	
Lorentzian width (eV)	0.19	0.21	

normalized spectra before and after a given annealing stage. We have used these surface components as a starting point for the deconvolution. In the next step, the linewidths, spinorbit splittings, and branching ratios were accurately determined by a fitting on the bulk lines for both elements, using the spectra of the clean surface. As a rule the same parameters were used for all surface components. As result of the fit, we could identify components characterized by the *same* chemical shifts, although their energies were let free in the deconvolution process. The only exception was for the broad A_2 and C_1 components, for which the chemical shift was not constant. The uncertainty was reduced by further imposing a constant energy difference between the volume contributions of the Ga and As core-level spectra.²¹

This procedure has allowed us to reproduce entirely all the core-level spectra with a very good accuracy for the two takeoff angles (deviations <1% and <3% for 0° and 70°, respectively). As a result, although a relatively large number of surface components is used for the annealing stages at low temperature, we are confident in our converging deconvolutions. The fitted curves, shown in the figures, are barely distinguishable from the experimental ones. The parameters used are shown in Tables I and II. The energy differences are given within 0.02 eV.

B. Interpretation of the surface components

The As 3d core-level spectra show the absence of chemical bonds with oxygen. Indeed, the corresponding surface component A_1 , which is known to lie at a larger binding energy, with a chemical shift of the order of 3 eV,^{12,22} is not detected. On the as-treated surface, one observes a broad peak, A_2 , which has lost the characteristic spin-orbit splitting. The maximum of this peak lies at a kinetic energy of 1.5 eV lower than the high-energy component of the volume contribution. We assign it to a mixture of sulfur-bonded arsenic and elemental arsenic. The composite nature of this peak is supported by the fact that, as can be seen in Fig. 4, the position and width of this peak change during the desorption of the passivating overlayer. The elemental arsenic signal, due to fourfold-coordinated arsenic-bonded arsenic, has been observed in many works and recent determinations agree on a relative binding energy of 0.6 eV.²³ Due to the large electronegativity difference between sulfur and arsenic, sulfur-bonded arsenic is expected to produce a peak at a larger binding energy. Such a peak has indeed been observed.^{12,22} As a function of passivation procedure, the position of the As-S peak can change by as much as 1 eV because distinct passivations produce different bond configurations. For the present passivation, Spindt et al.²⁰ have

As 3d						
	A_1	A_2	A_3	A_4	A_5	
Chemical shift (eV)		1.5-1.25	0.24	-0.28	-0.69	
Nature	absent	singlet (broader)	doublet	doublet	doublet	
Interpretation		As-S (partly)	excess As	dimers		
		Ga 3d				
	C_1	<i>C</i> ₂	<i>C</i> ₃	C_4	C ₅	
Chemical shift (eV)	1.28	0.98	0.75	0.35	-0.32	
Nature	singlet (broader)	doublet	doublet	doublet	doublet	
Interpretation		Ga-O	Ga-S	undimerized surface Ga	dimers	

TABLE II. List of the components used for deconvolution of the As 3d and Ga 3d core-level spectra, together with the chemical shifts with respect to the volume contribution, and our interpretation of these components.

found a broad line at a binding energy of approximately 1.5 eV above the bulk component.

The peak labeled A_3 lies at a relative binding energy of 0.24 eV. This peak is not due to sulfur-bonded arsenic on the ordered semiconductor surface, because it is observed on the clean surface. We attribute this peak to surface excess arsenic. Indeed, a surface component at the same position is found at the initial stages of decapping of arsenic-capped GaAs.^{18,24} It has been observed to decrease after annealing at 350 °C,¹⁸ and to disappear completely at 550 °C.²⁴ This is essentially what we find here, although we deal with a surface prepared in a different way. After annealing to 520 °C, we obtain a small residual signal, which does not significantly affect the present interpretation.

The peaks A_4 and A_5 , situated at a smaller binding energy, are also observed on the clean surface, and are therefore intrinsic. Peak A_4 , at a relative binding energy of -0.28 eV, will be assigned to arsenic dimers. The introduction of peak A_5 of smaller intensity, at a binding energy of -0.69 eV, improves the fit. Other workers find only one peak on the right side of the bulk contribution,²⁵ which lies at a relative binding energy intermediate between A_4 and A_5 , of the order of -0.45 eV. The peak A_5 is probably related with peak A_4 because, for several samples, its intensity seems to track its behavior. Second-layer arsenic can be ruled out by the results at a takeoff angle of 70°. There are several possible interpretations for A_5 : (i) undimerized surface arsenic, (ii) mixed As-Ga dimers, and (iii) arsenic dimers of a different type.

In the case of gallium, the dominant surface contributions are C_3 , C_4 , and C_5 . Peak C_3 is close to the Ga-S peak, which is found by other workers at a relative binding energy of 0.74 eV.¹² The two peaks C_4 and C_5 , which appear at a relative binding energy of 0.38 eV and -0.32 eV, lie close to structures generally observed on the clean GaAs surface. We assign C_5 to gallium dimers, and peak C_4 to undimerized gallium atoms.

At higher binding energies, the curves can be fitted using two very small additional peaks, labeled C_1 and C_2 . The C_1 peak has a relative binding energy of 1.28 eV with respect to the volume. This peak could have the same origin as the sulfur-related surface component found by others at a relative binding energy of 1.7 eV.¹² The C_2 peak has a relative binding energy of 0.98 eV with respect to the volume. We attribute this peak to oxygen-bonded gallium, in agreement with the known position of this peak, ^{12,26} and also because sulfide passivation is known to leave on the surface a residual oxygen concentration. However, the oxygen quantity is small because, in the valence-band spectrum, the characteristic structure due to oxygen¹⁸ is either not detected or buried in the sulfur signal.

V. INTERPRETATION

The deconvolutions of the core-level spectra support the qualitative analysis presented in Sec. III C, and give insight into the chemistry of sulfide passivation.

A. Sulfur desorption

For the annealing stage at 520 °C, the correlation between RAS and UPS is striking. After annealing, the valence-band spectrum suggests a clean surface.¹⁸ The appearance of gallium dimers found by RAS after annealing at 520 °C shows that gallium-related surface bonds are broken by this annealing. Whereas the gallium core-level spectrum remains essentially unchanged throughout the preceding annealing stages, peak C_2 disappears and peak C_3 is strongly decreased after this annealing. Thus, both for a takeoff angle of 0° and 70° , UPS shows that the annealing produces the breaking of surface Ga-S bonds and of the less numerous Ga-O bonds. On the other hand, there appears in the core-level spectrum a new peak C_5 , whereas the remaining peak C_4 slightly decreases. This very good correlation indicates that the C_5 surface component of the gallium core-level spectrum is due to gallium dimers.

After this annealing stage, some sulfur is still present, as the C_3 peak has not completely disappeared. However, whereas up to the preceding annealing stage, the Ga-Srelated component increases with takeoff angle, after this annealing stage, this component decreases with takeoff angle. Although we cannot exclude that steps on the surface can play a role, we think that some of this remaining sulfur has diffused underneath the surface. Such diffusion of sulfur atoms under annealing of the passivated surfaces was already mentioned in Ref. 27.

B. Breaking of arsenic-related chemical bonds

In the RA spectrum, annealing at 360 °C induces the arsenic dimer signal. Again, a correlated modification of the arsenic core-level spectrum occurs. Indeed, this annealing stage corresponds to the decrease of the peak A_3 and the increase of the peak A_4 , which is then related to arsenic dimers. The mechanism for the appearance of these dimers is not the same as for gallium dimers because, before this annealing stage, As-S bonds have virtually disappeared. The increase of this line is performed at the expense of the A_2 surface component, which is attributed to excess arsenic on the surface. This result shows that the appearance of arsenic dimers is not related to the breaking of possible As-S bonds on the surface, but of distinct chemical bonds such as those with excess arsenic. Note that this breaking does not induce any modification of the valence-band spectrum [curves 3(b) and 3(c)]. This may indicate that the excess arsenic which is desorbed does not induce a localized level in the valence band.

The above conclusion seems qualitatively valid, but the detailed picture of the system is probably more complicated. First, after the subsequent annealing stage at 520 °C, the A_4 component further increases, whereas the RAS line is attenuated and slightly shifted to a lower energy. This shows that a distinct phenomenon occurs, possibly related to arsenic desorption by annealing at this high temperature. This effect will not be interpreted here because it seems to depend on the details of the annealing procedure. For another sample,⁶ we find instead a much better correlation between RA signal and intensity of the A_4 component. Second, the deconvolution seems to reveal a small amount of As dimers on the as-treated surface (see top panel of Fig. 4). However, such a small component is close to the limit of the deconvolution precision, and also the corresponding As dimer signal in the RA spectrum would be too small to be distinguished from the background signal.

C. Chemistry of the passivating overlayer

The annealing stages at 150, 250, and 270 °C produce a progressive desorption of the passivating overlayer. Indeed, after annealing at 270 °C, the RA spectrum reveals the appearance of a line at 2.5 eV, due to dimerized sulfur atoms bonded to underlying gallium, and induced by desorption of overlying atoms embedded in the overlayer.^{4,5} Conversely, the valence-band spectrum becomes very similar to the one observed before the breaking of Ga-S bonds (curves b and c in Fig. 3).

This picture is also supported by the evolution of the corelevel spectra during the above annealing stages. The peak A_2 , mainly due to As-S chemical bonds, progressively decreases in the As 3d core-level spectra at 0° takeoff angle. This peak is very small after annealing at 270 °C and disappears completely after the 360 °C anneal. Thus, after the 270 °C anneal, there remains a small residual part of the overlayer. The rest of the surface is still covered by a monolayer of atoms, as seen from the absence of any significant arsenic or gallium dimer line in the RA spectrum [curve 1(c)]. The core-level spectra indicate that the galliumterminated part of the surface is covered with sulfur, and the arsenic-terminated one is covered by excess arsenic. This demonstrates that the As-S bonds are in the amorphous passivating overlayer and not on the semiconductor surface. This conclusion is supported by a photoemission spectroscopy analysis,²⁸ which has shown that, if the overlayer is removed by thorough rinsing of the surface, no As-S bonds are found and the Ga core-level spectrum is unchanged. Note that, at 70° takeoff angle, the situation is slightly different, as the A_2 line is still significant after the 270 °C anneal. As discussed below, this difference is related to the morphology of the overlayer.

On the other hand, sulfur forms chemical bonds with gallium atoms situated on the semiconductor surface and not in the passivating overlayer. The negligible concentration of Ga atoms in the passivating overlayer is indicated by the facts that (i) during desorption of the passivating overlayer, the intensity of the peak C_3 due to Ga-S chemical bonds in the gallium core-level spectrum, tracks the bulk contribution and the shape of the entire core-level spectrum stays unchanged, and (ii) all the surface components exhibit a similar increase at a takeoff angle of 70°, except the small broad peak C_2 (gallium bonded to oxygen), which has a relatively larger increase. The bonding of sulfur to surface gallium must involve a well-defined chemical configuration which, in agreement with theoretical calculations,²⁹ has been identified recently as Ga-S-Ga bridge sites.³⁰

The difference between Ga-related and As-related chemical bonds on the as-treated surface can be explained by the following picture. Using a general analysis of corrosion of *AB* compounds in alkaline solutions,³² and on the basis of electrochemical investigations,³³ the following reactions, which imply a participation of holes in the semiconductor, as well as OH⁻ ions in the solution, were proposed

$$GaAs + 3h^{+} + 6OH^{-} \rightarrow GaO_{3}^{3-} + As^{0} + 3H_{2}O,$$
$$As^{0} + 3h^{+} + 4OH^{-} \rightarrow AsO_{2}^{-} + 2H_{2}O.$$

The first reaction occurs first, since the more electropositive atom (gallium) is readily attacked by OH⁻ ions and dissolved into the solution.³² This is still true if sulfur-related ions such as HS⁻ are present in the solution since the reaction of gallium atoms with sulfur-related ions is slower than with OH^{-} .³⁴ For arsenic, on the other hand, the reaction with sulfur-related ions can be more efficient than chemical reaction with OH^{-.34} Thus, the second reaction is probably replaced by a more complex chemical process involving sulfur, which starts with a reaction involving As⁰, loosely bonded to the substrate. As shown by etching measurements,³⁵ these chemical reactions are further in competition with the formation at the semiconductor surface of a passivating layer consisting of sulfur irreversibly bonded to gallium in a bridgesite configuration and products of the chemical reaction between As⁰ and sulfur. This picture allows us to understand that (i) arsenic can be found under the form of elemental (or excess) As, or in the As-S form, (ii) As-S chemical bonds are located inside the passivating overlayer, and (iii) oxide is found under the form Ga-O rather than As-O.

The composition of the overlayer changes during desorption: after the first annealing stage at 150 °C, the spectra show the increase of the A_3 component due to excess arsenic, which is very pronounced at 0° takeoff angle, but is less marked at 70° takeoff angle. Thus, the desorption of the overlayer essentially removes sulfur atoms, whereas part of the arsenic atoms embedded in this overlayer become converted into excess arsenic at the semiconductor surface.

The morphology of the overlayer is also modified during desorption: unlike at 0° takeoff angle, the As-S component at a 70° takeoff angle does not change up to the 270 °C annealing, but disappears abruptly after subsequent annealing at 360 °C. The differences as a function of takeoff angle can be explained if desorption changes the morphology of the overlayer, which becomes patchy. At intermediate desorption stages, some parts of the surface are still covered by a relatively thick layer containing sulfur and arsenic. We think that such a patchy structure of the passivating overlayer reflects the roughness of the underlying semiconductor surface induced by the etching of GaAs(001) by $(NH_4)_2S_x$.³¹ Deterioration of the GaAs surface in alkaline solutions has been studied before:³⁶ for the GaAs(001) surface, the etching-induced roughness should be due to the removal of chains of atoms along the [110] direction, leaving sidewalls of (111) Ga stop-etch planes. Following Aspnes and Studna,³⁶ we assume that the surface of our sample consists of elongated facets. In our case, the importance of these facets can be stronger because of the 2° misorientation of the sample surface. We can explain our results if, during the first annealing stages, the overlayer desorbs more extensively from the top of these facets, leaving here excess arsenic. At this stage, the sidewalls are still covered and, at a takeoff angle of 70°, reveal a strong signal of As-S bonds. Thus, during desorption the initially thick and flat passivating overlayer takes the shape of such a faceted surface.

VI. CONCLUSION

Our UPS and RAS study of $(NH_4)_2S$ -passivated (001) GaAs as a function of annealing temperature yields two main results.

(a) We find that the three main annealing stages, which are desorption of the passivating overlayer, breaking of Asrelated and breaking of Ga-related chemical bonds, have correlated effects both on the UPS and RAS spectra. The desorption of the overlayer induces sulfur dimers on the gallium-terminated part of the surface, and the breaking of As (Ga)-related chemical bonds induces As (Ga) dimers. These three dimer types manifest themselves by characteristic signatures in the RA spectra. Using these results as a guide for the deconvolution of the UPS spectra, we find that, on sulfide-passivated surfaces, gallium dimers produce a surface component at a relative binding energy of -0.32 eV with respect to the bulk contribution, whereas arsenic dimers give rise to a component situated at a relative binding energy of -0.28 eV with respect to the bulk contribution. The deconvolution shows components due to sulfur respectively bonded to arsenic and gallium, but also components only observed so far on the clean GaAs surface, such as a component due to excess arsenic at a relative binding energy of 0.24 eV.

(b) Analysis of the results allows us to propose the following description of the chemistry of $(NH_4)_2S$ -passivated GaAs(001): For the as-treated surface, the semiconductor is covered by a protective overlayer which contains sulfur atoms and also all of the As-S chemical bonds that we observe in UPS. The interface between the semiconductor and this overlayer consists of essentially a monolayer of sulfur on the gallium-terminated part of the semiconductor surface, and of excess arsenic on the arsenic-terminated part of this surface.

Annealing up to 270 °C causes desorption of the overlayer. Sulfur atoms contained in this overlayer are desorbed, whereas some of the sulfur-bonded arsenic is converted into excess arsenic at the semiconductor surface. Analysis of the evolution of the core-level spectra as a function of takeoff angle suggests that the sample surface consists of facets along the [110] direction, produced by the orientationdependent etching of the surface by the sulfide-containing solution. We find that the excess arsenic is desorbed after annealing at 360 °C, which results in the appearance of arsenic dimers. The bonding of sulfur to gallium is performed in a well-defined site on the semiconductor surface. This is probably the Ga-S-Ga bridge site, for which the corresponding energy level is found lower than the top of the valence band.²⁹ These chemical bonds are broken by annealing at 520 °C, which reveals the clean semiconductor surface.

We shall show in the companion paper¹⁰ that the electronic properties of the passivated surface are essentially determined by the Ga-S chemical bonds and by the presence of excess arsenic.

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