

Surface core-level shifts of GaAs(100)(2×4) from first principles

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First-principles calculations show that measured surface core-level shifts (SCLSs) of the GaAs(100)(2×4) surfaces can be described within the initial state effects. The calculated As 3*d* and Ga 3*d* SCLSs for the β2 and α2 reconstructions of the GaAs(100)(2×4) surfaces are in reasonable agreement with recent measurements. In particular, the results confirm that both the lower and the higher binding energy SCLSs, relative to the bulk emission in the As 3*d* photoelectron spectra, are intrinsic properties of the GaAs(100)(2×4) surfaces. The most positive and most negative As shifts are attributed to the third layer As atoms, which differs from the previous intuitive suggestions. In general, calculations show that significant SCLSs arise from deep layers, and that there are more than two SCLSs. Our previously measured As 3*d* spectra are fitted afresh using the calculated SCLSs. The intensity ratios of the SCLSs, obtained from the fits, show that as the heating temperature of the GaAs(100)(2×4) surface is increased gradually, the area of the α2 reconstruction increases on the surface, but the β2 phase remains within the whole temperature range, in agreement with previous experimental findings. Our results show that the combination of the experimental and theoretical results is a prerequisite for the accurate analysis of the SCLSs of the complex reconstructed surfaces.

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I. INTRODUCTION

Surface core-level shifts (SCLSs) have been studied in solid state physics for many decades.¹⁻¹² The SCLSs are determined as a difference in the binding energy of the core-level photoelectrons emitted from the atoms that are located at the sample surface and deeper in the bulk. These shifts reflect the differences in the potential energy between separate atomic bonding sites. Thus, even if the core electrons are not involved in the chemical bonds, SCLSs provide useful information on the atomic structure of a surface. The SCLSs reflect different bonding sites of atoms in a surface structure. However, the deduction of the atomic structure from the observed SCLSs is not straightforward, and often interpretation of the atomic origins of the SCLSs relies on the intensity ratios of the components in the core-level photoemission spectra and on intuitive charge transfer picture, in which the relative gain (loss) of local electronic valence charge is connected to the decreased (increased) binding energy of the core levels. However, the peak intensities can frequently be affected by the diffraction effects, and the intuitive charge transfer picture is often too simplified, because it leaves out completely the changes in the interatomic Madelung potential. The Madelung potential is affected by several factors, especially including atomic coordination, charge transfer, and reconstruction. One should also note that different fac-

tors contributing to the SCLSs can tend to cancel each other. In other words, it is often difficult to link SCLSs and atoms in a surface structure without theoretical calculations.

An open question is still, whether SCLSs can be explained with the initial state properties of a surface, that is, whether the final state effects (i.e., response of other electrons to the creation of core holes) affect SCLSs. If such differences in the final state screening can be excluded or they cancel each other, then SCLSs provide direct information on the ground state properties of a surface. An answer appears to depend on the material examined. For example, the final state effects need to be taken into account in explaining SCLSs of some 4*d* metals^{10,13} (e.g., Pd and Rh) and Pd alloys,¹³ and of the elemental semiconductors Si and Ge,⁹ while SCLSs of III-V compound semiconductors (e.g., GaAs and InP) have been properly explained within the initial state picture.^{2,4-8,12,14-16} In metallic systems the screening of the core holes by conduction electrons is stronger than in semiconductors. Concerning semiconductors, it has been discussed that an energy band gap influences the proportions of the initial and final state effects in a simple way:^{9,12} the larger band gap, the larger initial state contribution. This is due to the less efficient and slower electronic relaxation in systems, which have larger energy gaps.¹² Thus, it can be expected that the initial state effects govern the SCLSs of the III-V(100) surfaces, as is the case for the III-V(110) surface.¹² The SCLSs of the III-V semiconductors have mainly been

studied for the (110) surfaces, but less is known about the physics of the SCLSs of the scientifically and technologically important III-V(100) surfaces, which usually undergo much stronger atomic rearrangements than the III-V(110) surfaces do. However, the SCLSs of the GaAs(100)(2×4), which is one of the most well-known semiconductor surfaces in general, are poorly understood. This issue is addressed here.

The As 3*d* spectrum of the GaAs(100)(2×4) surface has been observed to include at least one SCLS in addition to the bulk emission. Spectral fittings have revealed that this As 3*d* SCLS lies at 0.3–0.4 eV lower binding energy (BE) than the bulk emission (*B*).^{17–23} There is some variation in the reported values, but most of the experimental values are within the mentioned energy range.^{17–23} Recently, the As 3*d* emission from the GaAs(100)(2×4) has been found to include at least two SCLSs at about 0.2 eV higher and 0.3 eV lower BEs relative to *B*, respectively (third SCLS at around 0.6 eV higher BE than *B* was connected to extra As on the surface).²⁴ These two SCLSs of the GaAs(100)(2×4) have been tentatively related to different As dimers in the reconstruction (first layer and third layer dimers).²⁴ However, their atomic origins are still unresolved, and theoretical calculations are needed to get more detailed explanations for the As 3*d* SCLS. Furthermore, the Ga 3*d* emission from the GaAs(100)(2×4) surface has been found to include two SCLSs with the BE shifts of 0.3–0.4 and –0.25 to –0.35 eV relative to *B*,^{17–24} but their atomic origins are even poorly understood than the atomic origins of the As 3*d* SCLS.

II. CALCULATIONAL METHODS

The electronic structure calculations have been performed using the *ab initio* total energy program Vienna *ab initio* simulation package (VASP),^{25–28} which is based on the density functional theory.^{29,30} Within this package the projector augmented wave (PAW) method^{31,32} and the local density approximation of Ceperley and Alder,³³ as parametrized by Perdew and Zunger,³⁴ are used. The optimization of the atomic structure is performed using conjugate-gradient minimization of the total energy with respect to the atomic coordinates. The Ga 3*d*, 4*s*, and 4*p*, and the As 4*s* and 4*p* electrons are included as valence electrons. The GaAs(100)(2×4) $\alpha 2$ and $\beta 2$ structures are simulated by slabs. Slabs with 10 atomic layers (five As layers and five Ga layers) and 12 atomic layers (six As layers and six Ga layers) are used. Structural results differ from each other only very slightly (about 0.01 Å in interatomic distances). There are differences in the SCLS, which are 0.03 eV at maximum. Additional uncertainty in the SCLS is caused, because our bulk reference values are not strictly saturated, which means, that there is a small variation in the electrostatic potentials between the atoms in the bulk reference layers. The uncertainty in the SCLS due to this fact is estimated to be 0.03 eV, which, however, is partly included in the former uncertainty. The dangling bonds of the bottom surface Ga atoms are passivated by pseudohydrogen atoms³⁵ ($Z=1.25$). Theoretical lattice constant is calculated to be 5.603 Å, and two bottom

atomic layers of the slabs are fixed to the ideal positions. Other atoms, including the pseudohydrogen atoms, are relaxed until the remaining forces are less than 10 meV/Å. In fact, it is necessary to find proper positions for the pseudohydrogen atoms to get accurate SCLS. The third layer (Ga) and the fourth layer (As) of the bottom surface are considered as the bulk reference layers, which show bulk core-level reference energies due to the pseudohydrogen atoms. The energy cutoff is 350 eV. This plane wave cutoff energy was found to be sufficient for this study. The number of *k* points in the Brillouin zone is 8 corresponding to a *k* mesh of 2×4×1. Different *k* point samplings (2×4×1, 3×3×1, and 3×4×1) were tested with the smaller slab, and they affect considered physical quantities marginally. These points are determined by the Monkhorst-Pack scheme. The surface core-level shifts are calculated within initial state and final state models. The initial state shifts are evaluated by using the average electrostatic potential V_{atom} at the core of the Ga and As atoms, which is obtained by placing a test charge (ρ_{test}) with the norm 1, at each ion and calculating³⁶

$$V_{\text{atom}} = \int V(\vec{r})\rho_{\text{test}}(|\vec{r} - \vec{R}_n|)d^3\vec{r},$$

where the considered radii are 1.03 Å (Ga) and 1.06 Å (As). The initial state shifts were evaluated also by the eigenvalues of the core states.³⁷ Quite similar values are obtained by these methods for the initial state shifts of the Ga and As 3*d* core levels. Final state shifts, calculated within complete screening picture, include both initial state shifts and final state effects. In these calculations a single core electron is excited from the core to the valence by generating the corresponding core-excited PAW potential.³⁷ In the final state calculations only the screening by valence electrons is included. Final state calculations were performed only for the smaller slab.

Several tests were performed by using surfaces, for which theoretical SCLSs have been previously calculated. The SCLSs were calculated for the GaAs(110) and the Sb/GaAs(110). Values presented in literature are successfully reproduced. The calculated values are 0.15 eV for the Ga and –0.32 eV for the As [positive (negative) SCLS value means larger (smaller) binding energy] for the GaAs(110) surface, while the reported values in literature vary from 0.14 to 0.18 eV for Ga, and from –0.36 to –0.45 eV for As.^{10,12–14} Corresponding experimental values are 0.28 and –0.37 eV.² Our final state values –0.32 eV (Ga) and –0.56 eV (As) also follow the trend of Refs. 12 and 13 [–0.59 eV (Ga) and –0.76 eV (As)]. Our values for the core-level shift of the nonequivalent Sb atoms on the Sb/GaAs(110) surface are 0.36 eV in the initial state model and 0.33 eV in the final state model, while those of Ref. 38 are 0.41 and 0.37 eV. Experimental values vary between 0.40 and 0.45 eV.^{39,40} Conventional slab calculations were compared with the calculations, in which pseudohydrogenated slabs were used, and very similar SCLSs were obtained. Final state shifts for the 1×1 GaAs(110) and Sb/GaAs(110) surfaces were calculated by using 2×2 surface unit cells.

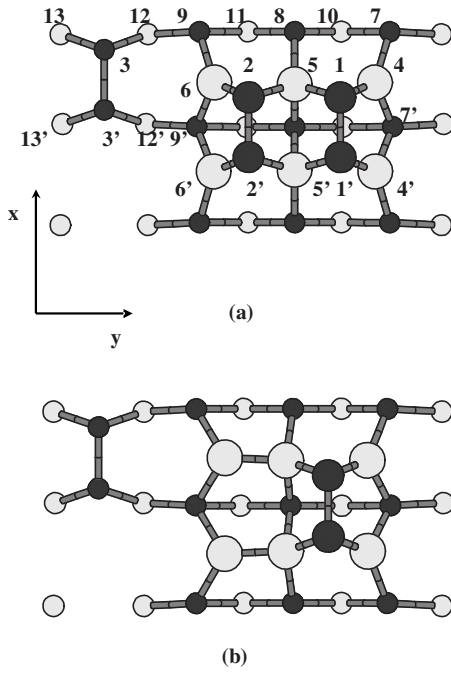


FIG. 1. Surface atomic structures of (a) $\beta 2(2 \times 4)$ and (b) $\alpha 2(2 \times 4)$ reconstructions of GaAs(100) (top view). The filled circles denote As atoms and the open circles denote Ga atoms. Atoms in the first and second layers are shown by larger circles.

III. RESULTS AND DISCUSSION

The GaAs(100)(2×4) $\beta 2$ and $\alpha 2$ reconstructions are shown in Figs. 1 and 2. The geometries of the considered reconstructions are presented by certain interatomic distances in the x , y , and z directions in Table I. The results are compared with the previously calculated values in Ref. 41 ($\beta 2$ structure) and in Ref. 42 ($\alpha 2$ structure). The notation of Miwa and Srivastava⁴³ is used. One can note good agreement between theoretical values given in this paper and those of Refs. 41 and 42.

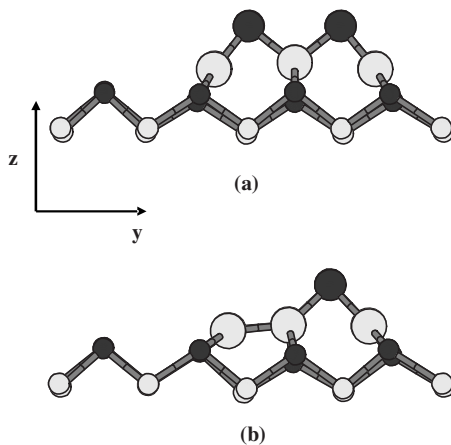


FIG. 2. Surface atomic structures of (a) $\beta 2(2 \times 4)$ and (b) $\alpha 2(2 \times 4)$ reconstructions of GaAs(100) (side view). The filled circles denote As atoms and the open circles denote Ga atoms. Atoms in the first and second layers are shown by larger circles.

TABLE I. Interatomic distances of the selected surface atoms of the $\beta 2(2 \times 4)$ and $\alpha 2(2 \times 4)$ reconstructions in x , y , and z directions.

	Distances (Å)			
	$\beta 2$	$\beta 2$ (Ref. 41)	$\alpha 2$	$\alpha 2$ (Ref. 42)
x direction				
As(1)-As(1')	2.48	2.50	2.48	2.47
As(3)-As(3')	2.48	2.50	2.50	2.50
Ga(4)-Ga(4')	3.69	3.65	3.70	3.67
Ga(5)-Ga(5')	3.55	3.52	3.70	3.68
Ga(6)-Ga(6')	3.69	3.65	3.91	3.88
Ga(13)-Ga(13')	3.73	3.70	3.72	3.71
y direction				
As(1)-As(2)	3.81	3.82		
As(2)-As(3)	6.01	5.92		
As(1)-As(3)	9.83	9.74	9.36	9.37
Ga(4)-Ga(5)	3.34	3.36	3.32	3.32
Ga(5)-Ga(6)	3.34	3.36	2.48	2.47
Ga(4)-As(1)	1.44	1.44	1.59	1.56
As(2)-Ga(6)	1.44	1.41		
z direction				
Ga(5)-Ga(4)	0.26	0.28	0.05	0.09
Ga(5)-Ga(6)	0.26	0.28	0.24	0.24
As(1)-Ga(5)	1.53	1.49	1.66	1.63

The SCLSs of the $\beta 2$ and $\alpha 2$ surface structures are given for the four topmost layers in Table II. One can note that there are many different shifts. The different SCLSs are collected into groups of energetically close shifts, and different groups are identified with different SCLSs in the following discussion. It is shown in Table II to which groups the different SCLSs belong to. Our first-principles calculations reveal four As $3d$ SCLSs with BEs around values of -0.27 [group I_{As}($\beta 2$)], -0.09 [II_{As}($\beta 2$)], $+0.15$ [III_{As}($\beta 2$)], and $+0.26$ eV [IV_{As}($\beta 2$)] relative to the bulk emission for the GaAs(100)(2×4) surface, which has the well-known $\beta 2$ (Refs. 41 and 44–49) structure. The As atoms directly below Ga atoms 12' and 13' in the fifth layer (two atoms) show a SCLS of -0.15 eV. Atoms below the fifth layer do not show significant shifts. These calculated SCLSs are in agreement with experimental observations, in particular, with those of Ref. 24, where the As $3d$ spectrum was found to include at least two SCLSs at -0.30 and $+0.17$ eV. Taking into account a rather poor experimental resolution and the fact that the minimal number of components were used to reproduce the As $3d$ spectrum,^{17–24} it is supposed that the -0.09 eV SCLS has not been resolved from the bulk emission, and that the $+0.15$ eV SCLS is not separable from the $+0.26$ eV SCLS in the measured As $3d$ spectra. It is also supposed that the -0.15 eV SCLS is not separable from the -0.27 eV SCLS in the measured As $3d$ spectra. The theoretical values are estimated to differ from the experimental ones within this picture about 0.1 eV or less. The same level of agreement is

TABLE II. Surface core-level shifts of the four topmost atomic layers of the $\beta 2(2 \times 4)$ and $\alpha 2(2 \times 4)$ reconstructions calculated by slabs of 12 atomic layers. Corresponding values for the smaller cell (ten atomic layers) are shown in parentheses. The individual SCLSs are collected into groups, which are denoted by Roman numerals. These groups are identified with the experimentally observed SCLSs.

Atom No.	SCLS $\beta 2$ (eV)		SCLS $\alpha 2$ (eV)			
First layer As						
1	-0.09	II _{As}	(-0.09)	0.08	II _{As}	(0.11)
1'	-0.09	II _{As}	(-0.09)	0.08	II _{As}	(0.11)
2	-0.09	II _{As}	(-0.09)			
2'	-0.09	II _{As}	(-0.09)			
Second layer Ga						
4	0.23	V _{Ga}	(0.23)	0.35	V _{Ga}	(0.38)
4'	0.24	V _{Ga}	(0.25)	0.37	V _{Ga}	(0.38)
5	-0.20	I _{Ga}	(-0.20)	-0.20	I _{Ga}	(-0.18)
5'	-0.20	I _{Ga}	(-0.20)	-0.20	I _{Ga}	(-0.18)
6	0.23	V _{Ga}	(0.25)	0.10	IV _{Ga}	(0.12)
6'	0.24	V _{Ga}	(0.25)	0.12	IV _{Ga}	(0.14)
Third layer As						
3	-0.27	I _{As}	(-0.27)	-0.26	I _{As}	(-0.25)
3'	-0.29	I _{As}	(-0.29)	-0.28	I _{As}	(-0.26)
7	0.26	IV _{As}	(0.27)	0.32	III _{As}	(0.35)
7'	0.01		(0.02)	0.11	II _{As}	(0.14)
8	0.15	III _{As}	(0.16)	-0.03		(-0.01)
8'	-0.24	I _{As}	(-0.24)	-0.27	I _{As}	(-0.26)
9	0.26	IV _{As}	(0.27)	0.01		(0.03)
9'	0.01		(0.01)	-0.04		(-0.01)
Fourth layer Ga						
10	0.08	IV _{Ga}	(0.08)	0.03		(0.06)
10'	-0.01		(0.01)	0.02		(0.04)
11	0.08	IV _{Ga}	(0.08)	-0.01		(0.01)
11'	-0.01		(-0.01)	-0.09	III _{Ga}	(-0.07)
12	-0.09	III _{Ga}	(-0.08)	-0.15	II _{Ga}	(-0.13)
12'	-0.15	II _{Ga}	(-0.15)	-0.16	II _{Ga}	(-0.14)
13	-0.08	III _{Ga}	(-0.08)	-0.05		(-0.03)
13'	-0.15	II _{Ga}	(-0.15)	-0.10	III _{Ga}	(-0.08)

found, if the most negative and most positive theoretical SCLSs would be taken to represent the experimental SCLSs. This is quite satisfying agreement, because even larger disagreement is found for the Ga 3d SCLS of the geometrically much simpler nonpolar GaAs(110) surface. Very accurate comparison between theoretical and experimental SCLSs is difficult, because there exist many shifts, which is not the case, e.g., on the GaAs(110) surface.

Experimental values are obtained from fits constructed using a minimal number of components deduced from the shapes of the spectra. If the number of components is wrong, the values of the SCLSs are affected. Therefore, it is important to know the theoretical SCLSs. One should also note

that the energy separation of about 0.45–0.55 eV of the most positive and most negative As SCLS is in good agreement with the experimental study of Ref. 24 (0.48 eV). In fact, taking into account several sources of errors in the experimental and theoretical results, it is not reasonable to expect best agreement for the individual shifts. Best agreement, however, is found in trends, and this is most important for the characterization of the surfaces.

The calculations show that the atomic origins of the -0.27 , -0.09 , $+0.15$, and $+0.26$ eV SCLSs are, respectively, the third layer As (atoms 3, 3', and 8'), first layer As dimers (atoms 1, 1', 2, and 2'), third layer As (atom 8), and third layer As (atoms 7 and 9) in the GaAs(100)(2×4) $\beta 2$ reconstruction. The calculated origins of the low BE shifts (negative SCLS) agree with previous tentative suggestions.^{17–24} For the high BE SCLS (positive SCLS), however, our results reveal significantly different atomic origin compared with those proposed in Ref. 24, where the high BE component was intuitively suggested to arise from the first layer As dimers. Indeed, this represents an example how speculative it can be to determine an atomic origin of SCLS without any theoretical support.

The final state SCLSs for the As first layer dimer atom 1 and third layer dimer atom 3 are -0.24 and -0.37 eV, respectively. These are rather close to the initial state values. However, the situation is different, if one considers atoms, which have positive SCLS. The SCLS of the third layer As atom number 9, e.g., is 0.26 eV in the initial state model, but -0.11 eV in the final state model. One could speculate that the final state contribution is properly attained only for the As dimer atoms within the complete screening. Although this is in principle a possibility, we argue that the final state contribution is small, because the trend is the same as in the case of the GaAs(110) surface. Final state calculations systematically decrease the SCLS and make all SCLS negative, including Ga SCLS. This casts a serious suspicion on all final state results of the GaAs surfaces. The final state model within complete screening fails mainly due to the overestimated screening of the core-electron holes of the surface atoms.⁵⁰ Of course, we cannot exclude a small final state contribution in the As 3d observations, but there is no reason to suppose that it could be obtained by the final state model within the complete screening picture otherwise than as an accident. It is clear that the initial state calculations described in all the experimental As 3d SCLS much better than the final state values, because the latter ones show no higher BE As 3d SCLS. A further convincing support to the initial state picture is obtained below by fitting previous As 3d spectra²⁴ of the gradually heated GaAs(100)(2×4) surface (Fig. 3). For these reasons only initial state results are discussed in the following.

We find five Ga 3d SCLSs corresponding to the SCLSs around -0.20 [group I_{Ga}($\beta 2$)], -0.15 [II_{Ga}($\beta 2$)], -0.09 [III_{Ga}($\beta 2$)], $+0.08$ [IV_{Ga}($\beta 2$)], and $+0.24$ eV [V_{Ga}($\beta 2$)] relative to the bulk on the GaAs(100)(2×4) $\beta 2$ surface (Table II). Their atomic origins are, respectively, second layer Ga (atoms 5 and 5'), fourth layer Ga (atoms 12' and 13'), fourth layer Ga (atoms 12 and 13), fourth layer Ga (atoms 10 and 11), and second layer Ga (atoms 4, 4', 6, and 6').

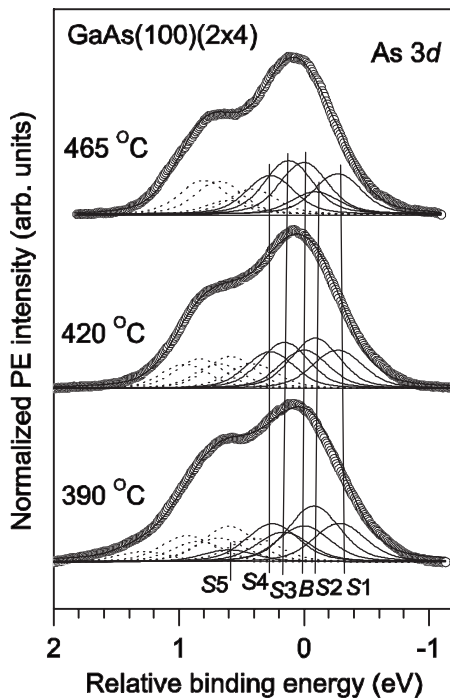


FIG. 3. Fitted As $3d$ core-level photoemission spectra from the GaAs(100)(2×4) surfaces heated at different temperatures. The photon energy is 90 eV and the emission angle is 60° from the surface normal. The vertical solid lines indicate the positions of the As $3d_{5/2}$ SCLS ($S1-S5$) and the bulk emission (B). The As $3d_{3/2}$ peaks are represented by dotted lines. The bulk emission determines the position of the 0 eV value.

These theoretical SCLSs agree again with previous observations.¹⁷⁻²⁴ Experimentally the most easily resolved SCLSs in the Ga $3d$ spectra are those around -0.20 and $+0.24$ eV (experimental values are -0.25 and $+0.31$ eV, respectively²⁴), which arise from the second layer, while the -0.09 and $+0.08$ shifts have been most likely too near to the bulk emission to be resolved in previous experiments.

Next, the SCLSs of the GaAs(100)(2×4) $\alpha 2$ surface (Fig. 1) are considered. For this surface, we find three As $3d$ SCLSs with BEs of -0.27 [group $I_{As}(\alpha 2)$], $+0.09$ [$II_{As}(\alpha 2)$], and $+0.32$ eV [$III_{As}(\alpha 2)$] relative to the bulk, of which atomic origins are, respectively, the third layer As (atoms 3, 3', and 8'), first layer As dimer (atoms 1 and 1'), third layer As (atoms 6 and 6'), and third layer As (atoms 4 and 4'). Two As atoms in the fifth layer show SCLS values of -0.15 and $+0.14$ eV. An interesting difference between the GaAs(100)(2×4) $\beta 2$ and $\alpha 2$ reconstructions is that the first layer As dimers show shifts toward lower and higher BEs on the former and latter surfaces, respectively. Otherwise, the SCLSs show quite similar trends on the $\beta 2$ and $\alpha 2$ reconstructions. The fourth layer Ga SCLSs are again small, and they are -0.16 [$II_{Ga}(\alpha 2)$] and -0.10 [$III_{Ga}(\alpha 2)$].

Let us now compare in more detail the previous theoretical SCLS to the experimental SCLS. To address that the calculated SCLSs describe well the measured core-level spectra of the GaAs(100)(2×4) surface, we have fitted afresh our As $3d$ spectra shown in Ref. 24 (Fig. 3). The bind-

TABLE III. The intensities of the different As $3d$ SCLSs ($S1-S5$) relative to the bulk emission (B) of the GaAs(100)(2×4) heated at different temperatures.

	S/B				
	$S1/B$	$S2/B$	$S3/B$	$S4/B$	$S5/B$
390 °C	1.07	1.54	0.82	1.06	0.33
420 °C	1.03	1.32	1.20	0.96	
465 °C	0.78	0.44	1.03	0.74	

ing energies of the $S1$ (surface component 1), $S2$, $S3$, $S4$, and $S5$ relative to the bulk emission B are -0.27 , -0.09 , $+(0.08-0.15)$, $+(0.26-0.32)$, and 0.6 eV, respectively. The $S5$ arises from an extra As on the surface, as described earlier,²⁴ while $S1-S4$ correspond to the calculated SCLS in Table II [$I_{As}(\beta 2)-IV_{As}(\beta 2)$ and $I_{As}(\alpha 2)-III_{As}(\alpha 2)$]. Based on previous studies,^{24,51} we can expect that the GaAs(100)(2×4) surfaces heated at 390–465 °C are composed of the $\beta 2$ and $\alpha 2$ structures, and that the concentration of the $\alpha 2$ structure increases as a function of the temperature. The allowed variations in the energetical positions of the $S3$ and $S4$ components reflect the presence of both phases on the surfaces. The $S2$ can be considered as an indication of the inclusion of the $\beta 2$ phase, although one As atom in the fifth layer causes a similar SCLS of -0.15 eV in the $\alpha 2$ reconstruction. Thus, comparison of the relative $S2$ intensities of the surfaces heated at different temperatures in Fig. 3 allows us to estimate the proportion of the $\beta 2$ phase as a function of the heating temperature: 0.92 at 420 °C and 0.46 at 465 °C (Table III), assuming that the surface heated to 390 °C is purely composed of the $\beta 2$ phase. These values nicely show the appearance of the $\alpha 2$ structure at higher temperatures, and that the $\beta 2$ phase remains within the whole temperature range, in good agreement with recent experiments.⁵¹ However, one should not take these values as a quantitative estimation of the $\alpha 2$ concentration.

Although qualitative agreement is found, the proposed atomic origin differs from the previous one.²⁴ In Table II one can note that there are some similar shifts in different layers. Therefore, the deduction of the atomic origins of the SCLS from the experimental data with simple geometrical and surface sensitivity arguments should be taken with proper caution. For example, the negative shift (around -0.27 eV), which is attributed to the third layer As dimer, arises also in the atom number 8'. According to the previous tentative suggestion the negative As SCLS should be connected to the first layer As dimers. However, theoretical results indicate that both the most negative and most positive As SCLSs arise in the third layer. Therefore, these experimentally most easily observed shifts are connected to the third layer.

Our results reinforce the fruitfulness of the combining of experimental and theoretical results in the analysis of the core-level photoemission spectra. This view has been maintained earlier in the literature,^{52,53} but it has been poorly demonstrated for semiconducting surfaces. This is rather surprising because semiconductors show a great variety of complex surface reconstructions, for which, especially, the deter-

mination of the SCLS forms an extremely useful scientific tool. One should note that, although significant SCLSs arise also from buried atoms in deep layers, these SCLSs strongly decrease in magnitude, if, for example, one considers artificial GaAs(100) surface with full Ga coverage. Thus, significant SCLSs arise also in deeper layers on the GaAs(100)(2×4) surface due to the geometrical structure of the (2×4) reconstructions.

IV. CONCLUSIONS

Reasonable agreement between the experimental and theoretical SCLSs, calculated within the initial state model, is found for the GaAs(100)(2×4) surface. The calculations confirm that there exist two groups of higher and lower BE As 3*d* SCLSs on the GaAs(100)(2×4) surface. The energy separation between these SCLSs agrees well with the recent measurements. This comparison is based on the experimental results, obtained by fitting the photoemission spectra with the minimal number of components. Although this method is generally reliable, a firmer basis for the accurate analysis of this complex reconstructed surface is obtained by the combination of the experimental and theoretical results, because experiments do not reveal the atomic origins of the SCLSs and do not necessarily reveal all SCLSs. This is shown by considering the atomic origins of the SCLSs and the intensity ratios of the SCLSs. The atomic origins of the most positive and most negative shifts are found to be in the third layer (and to a small extent in the fifth layer). This view differs from the previous suggestion, which was based on the experimental data only. New fits of the experimental spectra

with the theoretical positions of the SCLS show the appearance of the α_2 structure at higher temperatures, indicated earlier with independent experimental data. The success of this study encourages one to combine experimental and theoretical analyses in future studies of the GaAs-based surfaces. This is a big advantage, when the geometries of the less-known surfaces are investigated. Theoretical calculations support the previous statement, according to which the SCLSs depend sensitively on different kinds of factors. Therefore, *ab initio* calculations, instead of simple models, should be used to the interpretation of the experimental results.⁵²

Note added in proof. Our most recent calculations indicate that the pseudohydrogen atoms, used to passivate the dangling bonds, have a significant effect on the surface core-level shifts within the final state model. The preliminary SCLSs obtained within the final state model without pseudohydrogen have similar accuracy as the initial state SCLSs have when compared to the experimental values. Further investigations are needed to understand the origin of this effect. However the conclusions of this article are not affected by these findings.

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