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SiO_2 growth on GaAs by reduction of GaAs oxides: Separation of stoichiometric changes from SiO_2/GaAs band-lineup effects

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The deposition of Si on oxidized GaAs(110) surfaces produces the complete reduction of the GaAs oxides and the formation of SiO_2. These chemical reactions have been monitored *in situ* from synchrotron photoemission measurements. To discern the stoichiometry of the formed Si-oxide is a difficult task, because the Si(2*p*) core level shifts ~ 1.2 eV to lower kinetic energies during the chemical process. A detailed study of the system based on the comparison of the core-level binding energies and the work-function changes permits us to separate the interfacial voltage effects from the bonding charge transference and final-state relaxation contributions to the core-level shift. Thus, it can be concluded that the observed energy shift corresponds to a band-lineup variation at the SiO_2/GaAs interface, and that SiO_2 is formed from the beginning of the process. The band-offset variation is consistent with the decrease of an interfacial voltage related to an As excess produced in the first stage of the reduction of the GaAs oxides, and a tentative model is proposed. After the reduction of the substrate oxides, Si grows on the SiO_2 layer with a modification of 0.7 eV in the Si-SiO_2 chemical shift. Cluster size effects and band lineup at this interface are discussed as possible explanations.

INTRODUCTION

The growth of SiO_2 on GaAs by reduction of the GaAs oxides has been proposed as a way to obtain oxide/semiconductor structures.[1-3] The reduction of the substrate oxides occurs when Si is evaporated onto them, and the oxygen previously bonded to As and Ga atoms is transferred to the Si atoms. These reduction-oxidation reactions are expected from bulk thermodynamics. As a result, a Si-oxide/GaAs structure is obtained. This allows one to synthesize overlayers of oxides different from those of the substrate, and with superior insulating properties, on III-V semiconductors. Technological interest in this method depends on the density of electronic states present at the SiO_2/GaAs interface and on the Fermi-level pinning by these states. The deposition of Si, when the reaction is complete, produces the formation of a Si/SiO_2 interface in the opposite direction from the interface formed by thermal oxidation, and the formation of Si/SiO_2/GaAs structures.

This reduction-oxidation method permits one to obtain abrupt SiO_2/GaAs interfaces with very thin Si-oxide layers, and therefore surface techniques like photoemission spectroscopy (PES) can be used *in situ* to study the interface formation. Alternative SiO_2 deposition methods,[4] such as chemical-vapor deposition (CVD) or reactive sputtering, make it very difficult to obtain such thin layers, and the interfaces formed in that way are usually characterized by internal photoemission (IPE) or electrical techniques such as *C-V* or *I-V*, where the interpretations are not straightforward. In general, the position of the electronic levels at insulator/semiconductor interfaces are, by far, less well known than in the case of metal/semiconductor or semiconductor/semiconductor interfaces. Only the SiO_2/Si interface has attracted a great deal of both theoretical and experimental work. However, final agreement in the values of some fundamental parameters such as the band offsets, or even the band gap, has not been achieved.[5] The possibility of surveying our system with a direct method such as photoemission permits one to study in a detailed way the chemical changes occurring at the interface, to follow the energy variations of the GaAs and Si-oxide electronic levels at the SiO_2/GaAs interface, and to monitor the formation of the Si/SiO_2 interface.

In this work, the two interfaces of the Si/SiO_2/GaAs structure will be treated separately. During the formation of the SiO_2/GaAs interface, the chemical shifts of the Si-oxide spectra will be distinguished from the band lineup effects using the reference of three sets of electronic levels: the substrate core levels, the overlayer core levels, and the vacuum level. During the formation of the Si/SiO_2 interface, a variation in the relative energy position of the oxide and semiconductor is observed. The energy shift between Si and SiO_2 increases with Si deposition, leaving the Si-oxide thickness constant. This behavior appears different from the increase in the energy shift observed during the thermal oxidation of Si, which is explained in terms of a relaxation energy variation associated with the change in the permittivity with the oxide thickness. The results presented in this work will be discussed as band lineup and Si cluster size effects.

EXPERIMENT

Photoemission experiments were performed in an UHV system equipped with sample preparation and analysis devices, and attached to the TGM-3 beamline of the BESSY synchrotron facility. *p*-GaAs(110) samples, highly doped to minimize surface photovoltage effects ($Na = 1.7 \times 10^{18}$ cm^{-3}), were cleaved in the UHV system at a base pressure of 5×10^{-11} torr. The clean surface was characterized by low-energy electron diffraction

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(LEED) and photoemission to verify that a (1×1) reconstruction with less than 0.15-eV pinning was obtained. Complementary experiments were performed in the same synchrotron run with GaAs(100)-As-capped samples, under the same experimental conditions. The (100) samples were annealed in successive steps of increasing temperature showing different reconstructions, until Ga was segregated. In this way, the reference of metallic As and metallic Ga to the GaAs peaks was obtained. The binding-energy shift between metallic As and GaAs As($3d_{5/2}$) peaks was found to be 0.67 eV, and that between metallic Ga and GaAs Ga($3d_{5/2}$) peaks to be -0.82 eV.

After characterization of the clean GaAs(110)-(1×1) surface, the substrate was oxidized by means of electron-stimulated oxidation (ESO) at 150 eV. Using this method, an oxide layer ~ 8 Å thick, composed of As and Ga oxides, was formed. Si was deposited at very low rates, at a residual pressure lower than 1×10^{-9} torr, from a Knudsen cell. The calibration of the Si flux was obtained in a separate experiment when Si was deposited on a clean GaAs(100)-$c(8\times2)$ surface held at 600 K. At this temperature a layer-by-layer growth mode has been reported from the two first monolayers.[6] The attenuation of the Ga and As signals at low Si coverages was used with the exponential formalism to estimate the Si flux, giving a deposition rate of ~ 0.1 Å min^{-1}. The escape depths (λ) were chosen as 5 Å for the As($3d$) core level and 6 Å for the Ga($3d$) core level, that were recorded at kinetic energies of ~ 80 and ~ 100 eV, respectively. Details on oxidation and Si deposition procedures can be found in Refs. 1 and 2.

To monitor the chemical and electronic changes the Si($2p$), As($3d$), and Ga($3d$) core levels, and the valence band and cutoff, were recorded. The photon energy was determined to be 126.10 eV from measurements with the second-order light of the monochromator, and with a Gaussian full width at half maximum (FWHM) overall resolution of 350 meV. The cutoff measurements were performed biasing the sample to -10.00 V.

During Si deposition, the substrate was warmed in order to activate the diffusion of Si atoms[2] using a resistive heater placed inside the copper sample holder. The temperature was measured with a thermocouple fixed to an edge of the holder. Prior to the cleavage, a calibration with a second thermocouple in contact with the semiconductor surface was performed, revealing a uniform temperature in the system sample holder after a warmup time. During the chemical process, first the As oxides and later the Ga oxides are reduced. In order to avoid oxide desorption,[7] the sample was heated at 550 K until the reduction of As oxides was accomplished, and then the temperature was increased to 750 K. In this way the complete reduction of both As and Ga oxides is assured.

RESULTS AND DISCUSSION

When Si is deposited on oxidized GaAs surfaces, the sequential reduction of As and Ga oxides occurs with oxygen transfer to the Si atoms. Figure 1 displays a series of As($3d$) and Ga($3d$) spectra summarizing the chemical changes. From bottom to top the spectra corresponding to the clean surface, oxidized surface, and four stages of the reduction of the substrate oxides, denoted $a-j$ are shown. Throughout the whole work, the same steps of the process will be considered, and they will be denoted as $a-j$ when referring to experimental curves, and as $A-J$ when referring to points in a plot. Least-squares curve fitting to the experimental spectra was performed using Lorentzian shape doublets representing the mean lifetime broadening of the electronic levels, convoluted with Gaussian distributions including the experimental resolution and photon broadening. The fitting parameters are displayed in Table I. Figure 2 displays the Si($2p$) spectra corresponding to the different steps of the Si deposition. They show the first formation of a Si-oxide peak, and the subsequent appearance of the Si^0 peak. The decomposition of the Si($2p$) spectra is complex and requires a great deal of work, because the energy of the oxide peak is shifting and a reference level is lacking. A detailed discussion is made in the following paragraphs. The main conclusion that will arise is that most of the oxide corresponds to the SiO$_2$ stoichiometry from the beginning of the process. Therefore, the energy shift of the SiO$_2$ peak that appears in Fig. 2 corresponds to causes other than a stoichiometric variation of the Si-oxide.

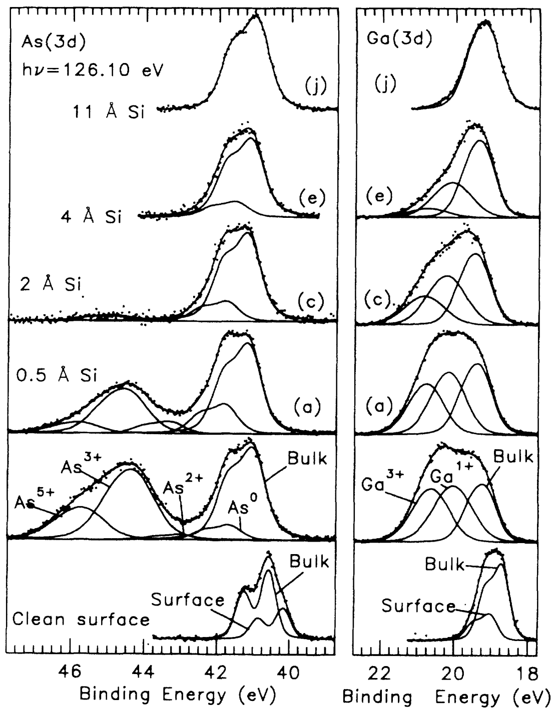

FIG. 1. As($3d$) and Ga($3d$) core-level photoemission spectra, after background subtraction, summarizing the reduction process of GaAs oxides by Si deposition. Curve decomposition illustrates the rise and fall of an elemental As-related component, which increases when the initial reduction of the As oxides results in an interfacial As enrichment. Curve-fitting parameters are displayed in Table I. All spectra are shown at the same height to illustrate more clearly the shape changes.

From Fig. 1 it is clear there is a faster reduction of the As oxides compared to the Ga oxides. The initial reduc-

TABLE I. Curve-fitting parameters of the Ga(3*d*) and As(3*d*) spectra at the clean surface and after oxidation. All energies correspond to binding energies, given in eV. The Gaussian FWHM represents the intrinsic values, not including the experimental resolution.

	Ga(3*d*)	As(3*d*)
Bulk energy at the clean surface	18.60	40.44
Spin-orbit splitting	0.45	0.69
Branching ratio	0.67	0.67
Lorentzian FWHM	0.15	0.17
Gaussian FWHM: clean (oxidized)	0.20 (0.40)	0.30 (0.50)
Surface component energy shift	0.29	−0.40

	Ga-suboxide	Ga^{3+}	As^0	As-suboxide	As^{3+}	As^{5+}
Energy shift	0.7	1.3	0.45/0.65	~2	3.1	4.5
Gaussian FWHM	0.60	0.70	0.50	0.75	1.10	1.30

tion of the As oxides produces an excess of As at the interface, which is compensated for by the subsequent Ga oxides reduction. The interfacial As enrichment contributes to the spectra as a component shifted between 0.45 and 0.65 eV to higher binding energy, i.e., close to the position obtained for metallic As, whose chemical shift related to the bulk GaAs peak was found to be 0.67 eV in a complementary experiment performed on GaAs(100)-As-capped samples under the same experimental conditions. This interfacial component related to As^0 is clear in the high-resolution photoemission spectra, although it could not be observed in previous measurements with conventional x-ray photoemission spectroscopy (XPS).[1,3] The chemical shift of the As^0 component increases with the amount of As atoms in excess, suggesting that low As enrichments do not show the metallic behavior which is obtained for higher densities of As atoms. The disappearance of the As^0 signal during the Ga-oxides reduction, and the observation of no component related to metallic Ga, supports the formation of a GaAs layer by the stoichiometric combination of the reduced components. Complementary experiments performed at room temperature provide evidence of similar behavior; therefore the disappearance of elemental As cannot be associated with thermal desorption. From the spectra of Fig. 1 it is also clear that the highest oxidation numbers are reduced first for both atoms. The last phase of the substrate oxides to disappear is thus the Ga suboxide.

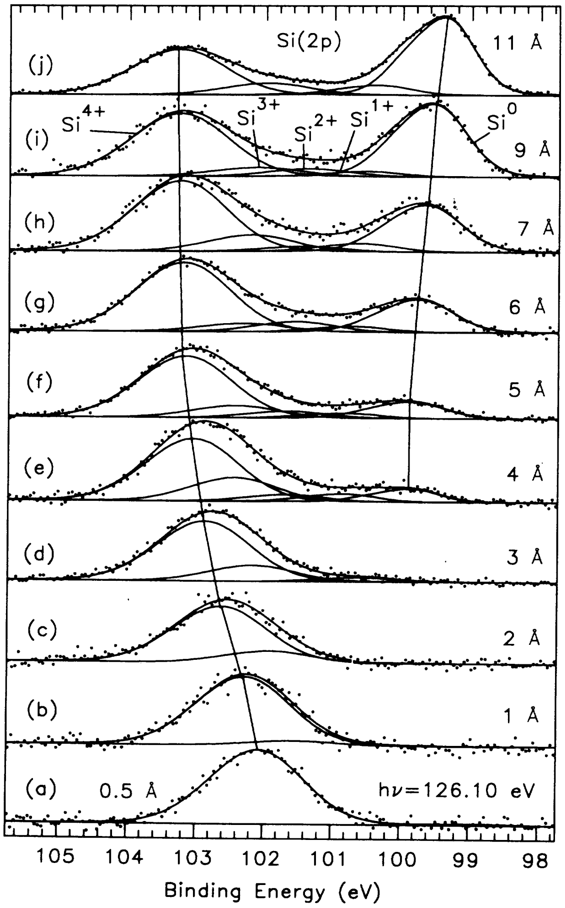

FIG. 2. Si(2*p*) photoemission spectra after background subtraction corresponding to Si deposited on an oxidized GaAs(110) surface. Curve-fitting details are explained in the text. All spectra are scaled to the same height to illustrate the shape changes more clearly.

A direct inspection of Fig. 2 shows clearly the first formation of Si oxides in curves *a*–*d*, and the latter appearance of elemental Si. From spectra *d*–*g* it is clear that formation of both elemental Si and SiO_2 is taking place. This fact stems from the development of the Si(2*p*) photoemission intensities of Fig. 3. These intensities correspond to the areas of the peaks of Fig. 2, normalized to the photon flux.

A major question concerning the deposited Si is the morphology of the Si oxide formed and also the final $Si/SiO_2/GaAs$ structure. It is important to know whether the Si oxide forms a continuous layer, and which is the growth mode of Si on the oxide at the end of the process. A previous work[2] observed the interruption of the reduction process at a certain stage, despite there being remaining Ga oxides. This fact is clear evidence that the synthesized SiO_2 forms a continuous layer, which impedes the Si atom from contacting the substrate oxides. Substrate warming during Si deposition was found to increase the amount of formed SiO_2 and reduced substrate oxides, suggesting that the process is controlled by Si diffusion from the surface to the GaAs oxide layer once

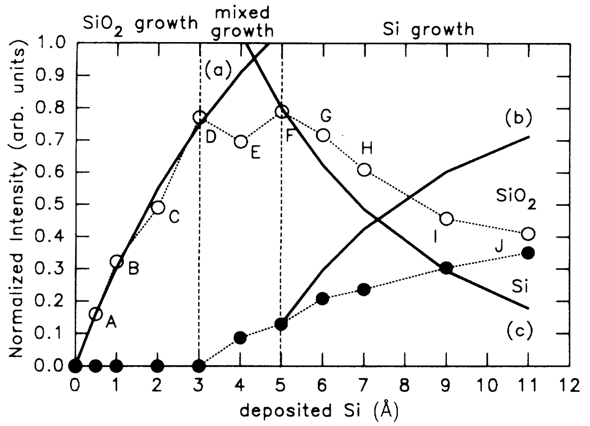

FIG. 3. Si(2p) core-level intensities of the Si oxide and elemental Si, normalized to the mirror current, determined from the area of the peaks of Fig. 2. The solid curves correspond to the fits of Eqs. (1) and (2) discussed in the text. Curve a is obtained with a λ value of 8.5 Å. For curves b and c, $\lambda=4$ Å is used.

the continuous layer of SiO$_2$ is obtained. Accordingly, the Si-oxide formation must present a layered growth. In order to verify this point and provide information about the growth mode of elemental Si, the photoemission intensities of the Si oxide and elemental Si plotted in Fig. 3 have been analyzed. The experimental values have been fitted to exponential growth and attenuation laws of the form

$$I(\theta)=I_{\infty}(1-e^{-(\theta/\lambda)}) , \tag{1}$$

$$I(\theta)=I_0 e^{-(\theta/\lambda)} , \tag{2}$$

Θ being the overlayer coverage, λ the electron escape depth, I_{∞} the intensity of a semi-infinite film of the overlayer material, and I_0 the intensity of the substrate before overlayer formation.

At the first Si deposition stages, curves a–d of Fig. 2, all Si atoms react with GaAs oxides to form Si oxide and, thus, only that oxide signal is present. The corresponding points A–D of Fig. 3 reveal an increase of Si-oxide intensity which agrees with the expected layered growth. The intensities can be fitted to Eq. (1) with λ values of about 8.5 Å, as corresponds to photoelectrons of ~20 eV from SiO$_2$,[8] and values of $I_{\infty} \sim 1.5$, consistent with the As and Ga intensities at the clean GaAs surface corrected by the photoemission cross section.

After ~6 Å of SiO$_2$ have been formed, a peak corresponding to elemental Si appears as well, and the reduction effects become slower until they stop. That corresponds to the coexistence of Si diffusion and nucleation of Si clusters. From points D–F of Fig. 3, both SiO$_2$ formation and Si growth are taking place, as the Si^0 signal increases simultaneously with a significant reduction of the Ga oxides. For the stage corresponding to point D, the As-oxide signal has already vanished.

From points F to I a small amount of Ga suboxide remains, which decreases with Si deposition. In this interval, the ratio of the Ga-suboxide intensity over Ga-GaAs varies from 0.2 to 0, corresponding to the reduction of the last ~0.5 Å of the remaining Ga suboxide and the formation of a similar or smaller quantity of SiO$_2$. Because the amount of SiO$_2$ formed in this region is only about 6% of the total, the SiO$_2$ thickness between points F–J is considered constant, and only Si formation is taken into account as an approximation to simplify the calculations. In Fig. 3, the SiO$_2$ signal is attenuated as the elemental Si signal increases in this region. An attempt to fit the attenuated SiO$_2$ intensities F–J of Fig. 3 to Eq. (2), and the corresponding Si intensities to Eq. (1) using a λ value of 4 Å, as has been reported for Si in the photoelectron energies considered,[8] shows a decay of experimental SiO$_2$ intensities, and a rise of the Si signal much slower than that expected for a layered Si growth. The simultaneous fit of the Si and attenuated SiO$_2$ intensities F–J, assuming a layered growth using other values of λ, is not possible due to the following facts. The fit of the SiO$_2$ intensities attenuated by the Si overlayer is only possible when a λ value of 8.5 Å is used. This value seems incorrect, because it is about twice that expected for Si, and it is not smaller than the λ used for SiO$_2$. One expects a smaller value of λ for the semiconductor than for its oxide in the energy range of the photoelectrons considered (~20 eV), due to the lack of low-energy losses in the wide-gap material. As regards the Si intensities, the relationship between I_{∞} for SiO$_2$ and Si in this energy range is ~1.7 according to Ref. 8. Under this condition, only a fit to the Si intensities with $\lambda=15$ Å is possible. This value is different from that found for the attenuation of the SiO$_2$ signal by the Si overlayer, and about four times the λ value expected for Si. From this we conclude that a layered model cannot explain the behavior of the photoemission intensities. The impossibility of curve fitting to a layered growth law is a clear indication that the growth mode for Si on SiO$_2$ consists of cluster formation. This result has been also confirmed by a separate Auger study.[9]

Once the morphology of the Si/Si-oxide/GaAs layered system has been clarified, the stoichiometry of the Si-oxide layer can be studied in a detailed way. In order to obtain the information needed the decomposition of Si(2p), the spectra of Fig. 2, using a least-squares-curve fitting method, has been attempted. The shape of the component curves has been modeled from a Lorentzian doublet with a 0.60-eV spin-orbit splitting, a 0.50 $2p_{1/2}/2p_{3/2}$ intensity ratio, and a 0.12-eV FWHM, convoluted with Gaussians of different widths for each component. Five components have been considered in the fitting procedure, corresponding to 0 to 4+ oxidation states. The photoemission work for the Si/SiO$_2$ interface performed by Himpsel and co-workers[8,10] will be followed in many parts of our analysis. From that work, an increase of the Gaussian FWHM with the oxidation number is clear. We have assumed a linear relation, and Gaussian widths of 0.7, 0.85, 1.0, 1.15, and 1.3 eV for the 0–4+ components have been obtained. In relation to the position of the different components, Himpsel and co-workers find the 1+ to 4+ oxides shifted 0.95, 1.75, 2.5, and 3.9 eV from the bulk Si. However, in the reduction-oxidation experiment discussed here, some differences may be expected as a Si/SiO_2 interface is formed instead of the usual SiO_2/Si obtained by oxidation of bulk Si. A major problem in the fit is the location of the suboxides, because they are not resolved and a reference level is lacking. When the Si atoms appear in the photoemission spectra, there is not a bulk Si^0 reference, but a Si-oxide peak whose binding energy moves to higher values as the process develops. In addition, the Si^0 peak, which appears in the spectra in an advanced stage of Si deposition, does not remain fixed, but moves to lower-binding-energy values. This Si^0 movement will be discussed later in terms of final-state relaxation effects related to cluster growth. The use of the Si^0 reference of the suboxides involves the assumption that the relaxation effects for the suboxides are the same as for Si clusters. Another possibility is to consider a hypothetical Si bulk component, which will be located in the position of the Si^0 peak of spectrum *j* or at a slightly lower binding energy, and whose energy remains constant throughout the process. The use of this fixed peak as a reference will mean a smaller contribution of the suboxide components to the oxide peak. Therefore, the use of the experimental Si^0 peak in each spectrum is an upper limit for the amount of suboxides, and a lower limit for the Si^{4+} intensity.

Accordingly, we have followed the criterion of using the experimental Si^0 peak in each spectrum as the reference, and of using as fixed values the suboxide chemical shifts reported by Himpsel and co-workers. For the Si^{4+} peak, the energy shift will be considered as a free parameter in the fit. Different values of the Si-SiO_2 chemical shift from ~3.5 to ~4.5 eV are usually reported for these oxide films of increasing thicknesses,[8,11,12] with the highest value corresponding to bulk SiO_2. This energy variation is usually explained in terms of relaxation effects due to the decrease of the permittivity with increasing oxide thickness, as the screening charge varies as $e(\varepsilon-1)/(\varepsilon+1)$.[13] If the Si(2*p*) core-level shift is separated into initial- and final-state energy shifts, a value of ~3.0 eV results for the initial-state contribution.[14] Eventually, final-state effects can increase the SiO_2 energy shift up to its value found for bulk material, 4.5 eV. Therefore, in ultrathin oxide layers where the extra-atomic relaxation contribution to the energy shift may be negligible, a lower limit for the Si-SiO_2 chemical shift will be 3 eV. Another explanation for the variation of the chemical shift is the possibility of band lineup modification at the Si/SiO_2 interface. The choice of varying Si-SiO_2 energy difference in the fit is consistent with both possibilities.

The decomposition of the final spectrum, curve *j* of Fig. 2, was performed first. This spectrum corresponds to the maximum amount of Si on the SiO_2 thin layer, and presents a chemical shift of 3.8 eV, which is similar to that observed for thin SiO_2 layers grown on Si substrates. A certain amount of suboxides are present as well. Curves *i*–*e* of Fig. 2 have been decomposed following the same method. They can only be fit using a major Si^{4+} component, although the Si-SiO_2 shift decreases as we approach the initial deposition stages. The decrease in the energy shift is due to ~0.25-eV movement in the Si-oxide peak toward higher binding energy, and ~0.45 eV in the Si^0 position in the opposite direction. In conclusion, the oxide peaks of curves *j*–*e* correspond mainly to the SiO_2 phase. The movement of the Si-oxide peak toward higher kinetic energies continues for the first steps of Si deposition.

For the first steps of Si deposition, spectra *a*–*d* of Fig. 2, where no elemental Si signal exits, the apparent Si-oxide position can in principle be attributed to either +4, +3, or+2 components, or mixtures of these oxides. The assumption of a larger amount of low oxidation index phases in the fitting will move the Si^{4+} peak to higher-binding-energy positions, so the determination of the Si-SiO_2 core-level binding energy requires knowledge of the oxide stoichiometry. Different possibilities of curve fitting have been tried with the separation among oxide phases fixed, and the whole spectra rigidly displaced in energy position. The energy shifts considered for the 1+ to 4+ oxide phases are those used for spectrum *e* of Fig. 2, the last with a Si^0 reference. They are 0.95, 1.75, and 2.5 eV for the suboxides, and 3.1 eV for the SiO_2, which is very close to the minimum shift expected for the SiO_2 thin-film layer. The results of a series of fits performed in this way for spectrum *c* of Fig. 2 are displayed in Fig. 4. The energy represented in the abscissa of Fig. 4 corresponds to the Si^0 peak, to which all other peaks are referred. The *x* axis is now given in kinetic energy, because in the forthcoming discussion the core-level shift will be compared with changes in the cutoff position, and it is more convenient to express the core-level shift in kinetic energies for a direct comparison. The stoichiometry corresponding to each fit is represented in Fig. 4(a). The quality of the different fits is represented in Fig. 4(b) by the value of chi square (χ^2). Reasonably good fits to the case discussed here are obtained for χ^2 values lower than 0.34. However, three best fits are possible, corresponding

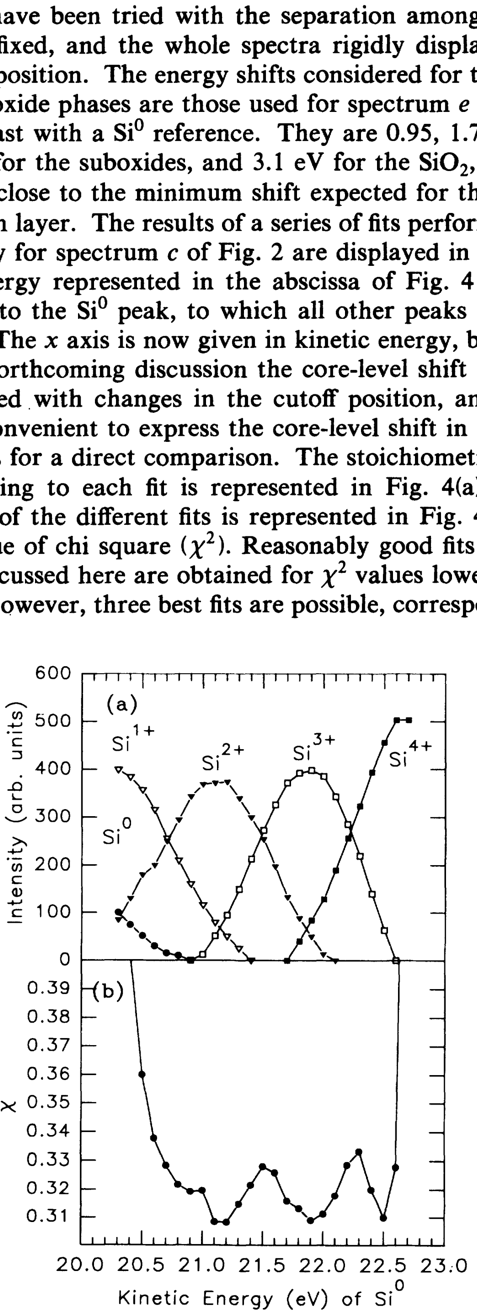

FIG. 4. (a) Stoichiometry corresponding to the possible fits of the spectrum displayed in Fig. 2, curve *c*. (b) χ^2 values of the fits as a function of energy position.

to nearly single phase oxides, and no choice can be inferred from only the Si(2*p*) spectra. The assignment of the solution to the minimum corresponding to a 4+ oxide gives an energy movement nearly identical to that of the apparent oxide peak, and it has been represented in the lower panel of Fig. 5 by curve *a*. Assignment to majority 3+ and 2+ oxides gives the SiO_2 energy position displayed in curves *b* and *c* of the same figure, respectively. For the 2+ oxide, possible fitting is limited to spectra *A* and *B*, and for the 3+ oxide a plausible fit is obtained for spectra *A*–*D*. The change from a minimum to other at a certain stage of the process cannot be excluded from these results. In the upper panel of Fig. 5, the kinetic-energy variation of the GaAs peaks is shown in order to provide evidence that the Si-oxide energy variation cannot be explained from the substrate band bending. In the inset of this upper panel, the same curve is plotted in the usual representation, i.e., as the Fermi-level position within the band gap.

Because the comparison of the energy variations of the Si(2*p*)–(Si-oxide) core level with the substrate core levels does not provide a solution to the coupled stoichiometric-electronic problem, similarities between the core-level movement and the vacuum energy variations have been examined. If the charge transfer from the Si atoms due to oxidation is maintained, then the electronic structure of the oxide will not change, and the distance from the core levels to the vacuum level must remain constant. Thus the vacuum level must remain parallel to curve *a* of Fig. 5, or present jumps if the transition from Si^{2+} or Si^{3+} to Si^{4+} takes place. The distance from the Fermi level to the vacuum level can be known from the position of the low-energy cutoff of the secondary electron signal. These measurements have been performed with the sample biased to −10.00 V, and are displayed in Fig. 6. In this plot, no double cutoffs are present, which supports the existence of a single oxide phase at the sample surface. The variation of the work function is shown in Fig. 7 with a solid curve. The values have been determined from the intersection of two straight lines, the constant background and the tangent to the secondary electrons fall of the curves of Fig. 6. Superimposed over the plot of the work-function variations is the movement of the substrate and overlayer core levels that were represented in Fig. 5. The energy variation of substrate core levels has only been plotted during oxidation. For the overlayer, curve *a* of the lower panel of Fig. 5 is shown. Direct comparison of the curve displaying

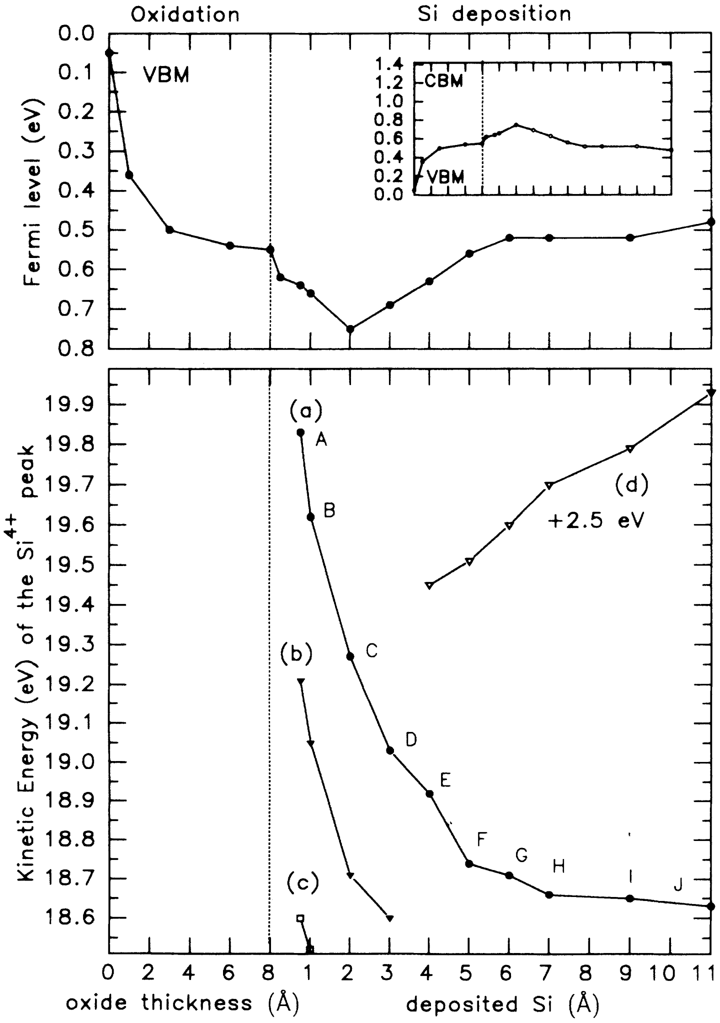

FIG. 5. Lower panel: energy position variations corresponding to the Si-oxide peak. Curve *a* corresponds to the position of the Si^{4+} peak under the assumption of a Si-oxide peak composed mainly of this oxide phase. Curves *b* and *c* display the Si^{4+} position assuming a majority +3 and +2 composition of the peak, respectively. Curve *d* shows the kinetic energy variation of the Si^0 peak; the kinetic energy of this peak is obtained adding 2.5 eV to the ordinate scale. Upper panel: Kinetic-energy variation of the GaAs peaks during the process, corresponding to band-bending changes. The ordinate energy scale represents the Fermi level referenced to the valence-band maximum. In the inset, these movements are represented in the conventional way, as the Fermi-level position within the band gap.

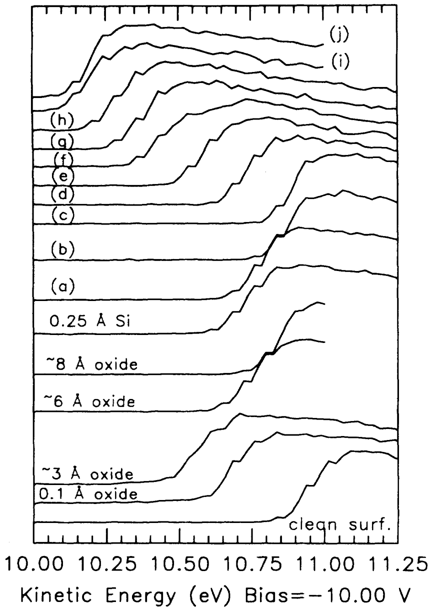

FIG. 6. Cutoff of the electron distribution curves measured with the sample biased at −10.00 V, displacing the work-function variations.

the Si-oxide movement with the work-function variation shows the rigid shift of the electronic structure of the SiO$_2$, as the distance from the Si core level to the vacuum level is maintained constant from points *C* to *J*. This shows that no stoichiometric changes affect the Si-oxide layer in this interval, and that final-state relaxation effects are not responsible for the observed shift of the Si-oxide peak. This conclusion does not change if the chemical shifts of the suboxides are lower than those used in the fit. We can conclude that the combination of the fitting analysis method with the comparison of the vacuum level position excludes the existence of a relevant amount of suboxides in any simple structural model. However, it must be taken into account that to our knowledge the present results are the first concerning the work-function definition of an ultrathin oxide layer, and so unexpected complicated structural situations cannot be excluded.

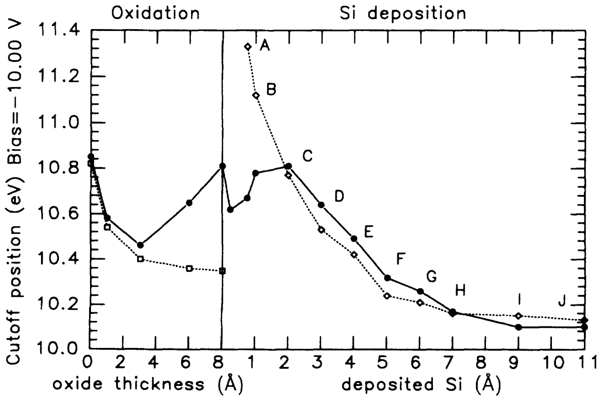

FIG. 7. Work-function variations determined from the cutoff curves of Fig. 6. As a comparison, the substrate band bending during oxidation and the SiO$_2$ movement of Fig. 5 curve *a* is represented in dotted lines.

The separation of the work function and the Si-oxide curves for points *A* and *B* of Fig. 7 can be due to stoichiometric changes from a +4 to a +3 Si oxide, or variations in the work function due to the transition from the GaAs-oxide bands to the SiO$_2$ bands. No experimental evidence for either of the two possibilities can be given, although the smooth continuation of curve *a* of Fig. 5 makes it very tempting to believe in +4 oxide formation from the very beginning. This can be expected, because the first deposited Si atoms arrive at an oxygen-rich amorphous GaAs-oxide surface. Therefore a huge strain is not expected, as in the case of initial Si/SiO$_2$ formation, where a large mismatch between the Si lattice parameter and the oxide bonding distance strains the interface and disables the formation of SiO$_2$ for the first monolayer. A very interesting point is that Fig. 7 gives strong support to the conclusion that the SiO$_2$ electronic structure is attained at point *C*, for an oxide thickness of about two monolayers.

Thus the difference in the movements of the GaAs substrate and the Si-oxide overlayer core levels is due to the modification of the band offsets at the insulator/semiconductor interface. Accordingly, the electronic movements displayed in Fig. 7 can be interpreted consistently. During the first steps of oxidation of the GaAs substrate, the Fermi level moves from the valence-band maximum (VBM) to a pinning position situated 0.45 eV above it, remaining parallel to the GaAs core levels and the vacuum level. Further oxidation continues the semiconductor pinning to 0.55 eV, but an increase in the work function occurs in the meantime that separates the core level from the vacuum level movement. Several additional experiments have confirmed that over a thickness of ~5 Å of the GaAs-oxide layer, a rise in the work function takes place which is related to the formation of the band structure of the GaAs oxides. The first steps of Si deposition produce an upward movement of the Fermi level in the semiconductor midgap, and an erratic behavior of the work function. That can be understood as the transition from a GaAs-oxide band to a SiO$_2$ band structure in the surface region. After this transition region, and once a SiO$_2$ layer fully covers the sample, the work function of the SiO$_2$ appears to be well defined, and complete agreement is found between the vacuum level and the movement of the Si(2*p*) core level of the SiO$_2$.

Figures 5 and 7 show the movement of the SiO$_2$ electronic structure with reference to the electronic levels of the GaAs substrate. This movement is simultaneous with the disappearance of the As excess produced in the first stages of GaAs-oxide reduction that was pointed out in the discussion of the Fig. 1. Actually, point *C* of Fig. 5 corresponds to about 1 ML (monolayer) of As enrichment at the interface. Due to the amphoteric character of the As atoms, the electronic charge can be transferred from the GaAs substrate to the SiO$_2$ overlayer, leaving a neutral total charge. Therefore, the elemental As is expected to play a role similar to an intralayer in the band lineup of semiconductor structures. A dipole layer related to the As excess, with the positive charge at the GaAs side and the negative at the SiO_2 side of the interface, will produce an interfacial voltage which increases the conduction-band offset between substrate and overlayer, and will vanish when the As excess is compensated for. A model based on this relation can be considered only as plausible. The main difficulty is that we are not dealing with a well-ordered semiconductor epitaxial structure, but with an amorphous SiO_2 overlayer on top of a GaAs substrate covered with Ga oxides and elemental As at certain stages of the process. In spite of the complexity of the actual situation, a model based on an As intralayer can provide a qualitative explanation, as follows.

The main hypothesis of the model is to consider the As atoms previously bonded to oxygen, linked after reduction to the GaAs and SiO_2 terminating layers, forming thus two interfaces: GaAs/As and As/SiO_2. This situation is shown in the simplified scheme of Fig. 8. Let us consider these two interfaces separately. For the GaAs/As interface, the presence of As excess in the vicinity of the nonpolar GaAs(110) surface induces a decrease in the negative charge of the As atoms of the last semiconductor layer, resulting in a net positive charge that can be estimated as follows. In bulk GaAs, each As atom attracts electronic charge from the more electropositive Ga atoms through the four Ga-As bonds. The amount of electronic charge transferred per bond has been determined to be $\sim 0.1e$ from theoretical calculations.[15,16] For the Ga atoms in the last semiconductor layer, a new bond with the interfacial As is formed, so no significant changes in the charge transfer occur. However, the As atoms of the last GaAs layer are positively charged when compared to the As atoms in bulk GaAs due to the lack of one polar As-Ga bond. Therefore, the originally nonpolar (110) surface becomes positively charged in the presence of As atoms, which results in a surface charge density $\sim 0.07\ \mathrm{C\,m^{-2}}$. For the As/$SiO_2$ interface, the formation of a negatively charged layer can be explained assuming that oxygen atoms bridge both materials. Estimations of the charge transferred for an As-O bond in As_2O_3 range from $0.3e$ to $0.4e$.[17] For the case of SiO_2, it is known from theoretical calculations that there exists a relationships between the Si-O-Si angle and the charge transference.[18] This angle can vary from 90°, as would correspond to pure p orbitals of the oxygen atoms, to 180°, which is found in the β-cristobalite allotropic form. In α quartz it takes a value of 144°, and this is also the average angle in an amorphous structure. The values of the charge transference per bond calculated by Harrison[18] are $0.26e$ for a 90° angle, $0.36e$ for 144°, and $0.60e$ for a 180° angle. The values of the charge transference for As-O and Si-O bonds are very similar, and therefore a slight increase of the As-O-Si angle from the average value is enough to produce a net negative charge of $\sim 0.1e$ in the bridging oxygen atom, which compensates the positive charge induced at the other interface.

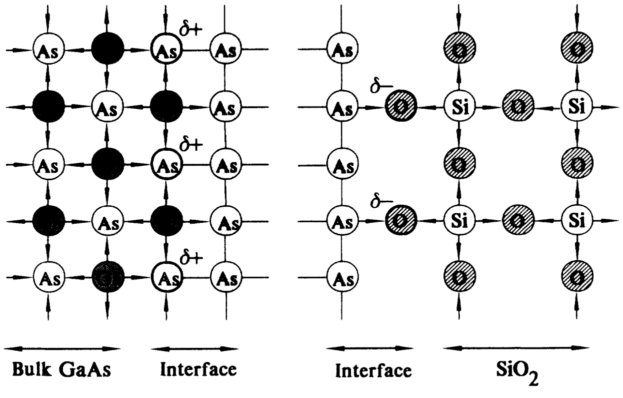

FIG. 8. Simplified noncrystallographic bonding scheme of the effect of As enrichment at the GaAs/SiO_2 interface. The As excess is modeled by the formation of two interfaces GaAs/As and As/SiO_2, in which positive and negative charges are induced. The arrows represent the charge transfer in polar bonds.

The positive layer situated in the termination of the GaAs, and the negative in the edge of the SiO_2, can be considered as two charge sheets separated by a neutral As intralayer. An interfacial voltage estimation can follow in the same way as has been used for III-V semiconductor heterojunctions,[19] where simple calculations have been proven to provide a reasonable approach.[20] The interfacial voltage will vary as $V = \sigma d / \varepsilon$, d being the intralayer thickness, σ the surface charge density, and ε the permittivity. Some estimation of the interfacial voltage can be made. As a rough approximation, we can use the value of the permittivity of the GaAs substrate, 13.1, for the $As^{\delta+}$-As bond, assuming a GaAs bonding distance of 2.45 Å and a SiO_2 permittivity of 3.9,[21] for the As-O bond, assuming an As_2O_3 bonding distance, of 1.80 Å.[22] Considering a charge density of $0.07\ \mathrm{C\,m^{-2}}$, this results in a interfacial voltage of 0.51 V for one As monolayer. The agreement is reasonable with the change in voltage observed when the As monolayer is depleted. The model assumes that the Ga_2O_3 remaining at the interface plays no role in the surface charge induction, and thus it is not specifically included. Other possibilities for the interfacial atomic arrangement may be expected, although the framework of the interpretation remains essentially the same. For instance, if the elemental As atoms are mainly distributed in the vicinity of the GaAs substrate, the formation of a surface negative charge layer at the SiO_2 side of the interface can be explained in the same terms for a Ga-suboxide/SiO_2 interface, with oxygen atoms bridging the Ga and Si atoms.

We turn now our attention to the energy shift of the Si^0 peak displayed in Fig. 5 (curve d). The energy variation in the position of this peak is ~ 0.45 eV, in a direction opposite to the ~ 0.25-eV oxide movement, and results in a total Si:SiO_2 energy difference increase from 3.1 to 3.8 eV with augmenting Si coverage. The increase of the chemical shift occurs for a nearly constant SiO_2 thickness, as the reduction process is almost exhausted from curves f to j of Fig. 2. Therefore, the common explanation[8,14] for the chemical shift change at the interface obtained from SiO_2 thermal oxidation of Si substrates, based on the variation of the oxide thickness, is not viable here. Two possibilities can be considered to account for the change in the energy shift. The first arises from the fact that Si does not follow a two-dimensional growth mode but forms clusters on top of the Si oxide, as was deduced from the discussion of Fig. 3. The second possibility is a modification of the band lineup at the Si/SiO$_2$ interface.

The effect of Si cluster growth on the energy shift of the Si($2p$) core level can be understood as a variation in the extra-atomic relaxation energy of the core hole produced in the photoemission process. This relaxation energy variation is due to a modification of the electronic structure of Si clusters with cluster size. Theoretical works predict an enlargement of the band gap for semiconductor clusters that varies in proportion to the inverse square of the mean diameter.[23] This fact is reflected in the elementary excitations, and has been proven experimentally as a photoluminescence blueshift[24] or a plasmon energy increase of ~ 0.5 eV with decreasing cluster size.[25] The relaxation energy can be expressed as[26,27]

$$E_{\text{relaxation}} = \frac{1}{2}\left[1 - \frac{1}{\varepsilon_{\text{st}}}\right]\frac{e^2}{r} , \tag{3}$$

r being the radius of the dielectric environment and ε_{st} the static electronic dielectric constant. If the value of r is maintained, the observed core-level shift variation of ~ 0.7 eV will correspond to a decrease of the permittivity from 11.9, i.e., the value for bulk Si, to 6. The value of the static permittivity ε_{st} can be related to the Si cluster mean diameter, according to the equation

$$\varepsilon_{\text{st}} = 1 + \frac{2n\,[d_{0e}]^2}{\varepsilon_0}\,\frac{1}{1.12 + \dfrac{2\pi^2\hbar^2}{m^* d^2}} . \tag{4}$$

This expression can be obtained from the dependence of the dielectric function with the band gap of Eq. (5), and the gap dependence with the mean cluster diameter of Eq. (6):[25]

$$\varepsilon(\omega)_{\omega \to 0} = 1 - \frac{ne^2}{\varepsilon_0 m}\,\frac{f}{\omega^2 - \omega_g^2} , \tag{5}$$

$$E_g = 1.12 + \frac{2\pi^2\hbar^2}{m^* d^2} , \tag{6}$$

n being the number of electrons per unit volume, m the mass of an electron, m^* the electron effective mass in bulk Si, $\hbar\omega_g$ the energy gap, ε_0 the vacuum permittivity, and f the oscillator strength. This last parameter can be expressed as[25]

$$f = \frac{2mE_g}{e^2\hbar^2}[d_{0e}]^2 \tag{7}$$

d_{0e} being the atomic dipole matrix element for the excitation, which is assumed to be independent of the cluster size as it is an intrinsic atomic factor. According to these equations, the change of ~ 0.7 eV in the relaxation energy corresponds to an initial Si cluster diameter of ~ 10 Å. This appears a reasonable value for the first stages of growth in a nucleation-based process. Therefore, the three-dimensional growth of Si agrees semiquantitatively with the observed energy shift.

A second explanation for the energy shift of the Si($2p$) core level is the possibility of band lineup variations at the Si/SiO$_2$ interface during its formation. These variations can be expected from the results of several previous works. Himpsel *et al.*[8] provide a value of the valence-band offset (VBO) of 4.3 eV using PES measurements, and mention that a smaller value is found for oxide layers thinner than 5 Å. Perfetti *et al.*,[28] with PES techniques, find a VBO of 4.9 eV for the interface obtained by evaporating Si on a SiO$_2$ layer, and they to modify this value to 5.15 and 4.4 eV by inserting Cs and H intralayers, respectively. IPE techniques performed for thicker oxides give a value of 3.2 eV for the conduction-band offset (CBO);[29–31] therefore the corresponding VBO is obtained by subtracting the Si band gap (1.1 eV) and the CBO from the SiO$_2$ band gap. Usually a value of 9.3 eV for the SiO$_2$ energy gap is considered,[32,33] which results in a VBO around 5.0 eV. From these works it seems clear that the VBO can take values ranging from 4 to 5 eV, with the lower values corresponding to thin overlayers. Our observation of the Si-SiO$_2$ core-level energy shift increase can be interpreted coherently as an increase of the VBO around 0.7 eV with increasing Si coverage. Accordingly, the band lineup seems to form here for a certain thickness of the Si or SiO$_2$ overlayers, suggesting the extension of the interfacial electronic structure to several monolayers at both sides of the interface.

At present, no definitive evidence for either of the two mechanisms discussed for the energy shift of the elemental Si peak can be given, even if both occur simultaneously. However, experimental results support the existence of a three-dimensional Si growth, and this justifies the core-level energy variation. Following that, the second mechanism appears to play a secondary role in the energy shift.

CONCLUSIONS

The deposition of Si on oxidized GaAs substrates produces the formation of continuous SiO$_2$ layers. The comparison of the vacuum level variation with the movement of the Si($2p$) core level of SiO$_2$ allows for the separation of chemical shifts from the rigid energy shift of the electronic structure. This analysis reveals that SiO$_2$ and not Si suboxides are formed from the beginning of the reduction process. The electronic structure of the SiO$_2$ overlayer is obtained at a thickness of about two monolayers. A significant movement of the SiO$_2$ electronic structure relative to the GaAs substrate is observed simultaneously with the depletion of ~ 1 ML of As interfacial enrichment. An interfacial dipole model can explain the modification of such an interfacial voltage. A variation in the Si-SiO$_2$ energy is observed when Si island growth occurs on the SiO$_2$ overlayer. This effect can be explained by extra-atomic relaxation energy variation related to the cluster size, or by a band lineup change due to a dipole structure distributed in an extended Si/SiO$_2$ interface.

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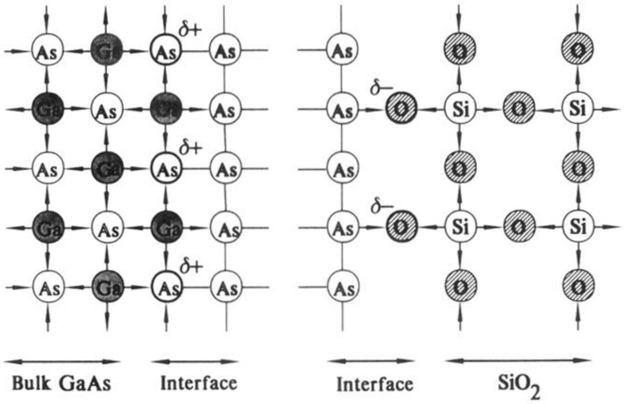

FIG. 8. Simplified noncrystallographic bonding scheme of the effect of As enrichment at the $GaAs/SiO_2$ interface. The As excess is modeled by the formation of two interfaces GaAs/As and As/SiO_2, in which positive and negative charges are induced. The arrows represent the charge transfer in polar bonds.