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Ab initio calculations of soft-x-ray emission from Si(100) layers buried in GaAs

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Calculations of soft-x-ray emission spectra from Si(100) layers buried in GaAs are reported. The local densities of states for Si in As and Ga sites are found to be very different. By comparison with experimental data, this difference allows us to determine the relative amounts of Si in the two types of sites. In the case of a single Si layer we find that 63 (±5)% of the buried atoms are in Ga sites. [S0163-1829(98)11139-6]

I. INTRODUCTION

In comparison with surface and bulk systems, knowledge of the electronic states in interlayers and at interfaces is relatively limited. The reason for this is that conventional spectroscopical methods are not particularly useful in this context. Bulk methods, like optical absorption, are not sensitive enough to give information about the relatively small interface volume. Surface sensitive probes, e.g., photoelectron spectroscopy, on the other hand, can only probe external surfaces. However, knowledge of the electronic structure of interfaces is crucial for understanding any device properties.

Recently it was demonstrated[1] to be feasible to map the details of the electronic density of states in deeply buried ultrathin layers using soft-x-ray emission (SXE) spectroscopy. Irradiating the sample by a very brilliant source, e.g., a dedicated synchrotron beamline, it is possible to detect characteristic fluorescence from buried layers. Spectra were reported from 1 and 3 ML of Si deposited on undoped GaAs(100) and overgrown with 100-Å GaAs. The overgrowth was performed at a relatively low temperature (500 °C) in order to suppress Si/GaAs intermixing.

In this paper we analyze the experimental findings by calculating *ab initio* SXE spectra for different model systems. At low concentrations, Si atoms are known[2] to be incorporated substitutionally in Ga sites. Outside the range of normal doping concentrations, the situation becomes increasingly complex,[3,4] with higher Si content. Reduced mobilities and free-carrier concentrations indicate that As sites become substituted, and Si-rich domains (even segregation) occur. In the experiments at hand there is currently no detailed knowledge of the microscopic distribution. We have therefore chosen to consider some alternative model arrangements. Two types of geometries have been treated: (i) a ''segregated model,'' where it is assumed that the Si atoms form ideal (100) planes of one type (either anion or cation sites); and (ii) a ''mixed model,'' in which case the Si atoms occupy random anion and cation sites. The case of three Si(100) layers is treated only within the segregated model, since the relative importance of mixing should be reduced because of the increased thickness. Preliminary results mainly considering the segregated model for 1-ML Si in GaAs(100) have been published in another report.[5]

II. THEORY

All wave functions and energy eigenvalues were calculated *ab initio* within density-functional theory[6,7] (DFT) using the local-density approximation (LDA) implemented as in Refs. 8 and 9. For the electron-ion interaction, fully separable, nonlocal pseudopotentials (PP's) were used,[10,11] based on self-consistent solutions of the relativistic Dirac equation for free atoms.[12–14] The calculations were performed using the plane-wave band structure code fhi94md.cth,[15] which is a heavily modified version of fhi93cp,[16] which concerns the computational methods. The geometries were described by the slab supercell method, using the theoretical lattice constants for GaAs (5.50 Å) and Si (5.39 Å) in all calculations.

To describe the single Si(100) layer, we placed 1-ML Si inside a seven-layer GaAs slab. The system (supercell) was then periodically repeated. Four different geometries were explicitly considered, two within the ''segregated model'' [Figs. 1(a) and 1(b)] and two with ''mixed'' distributions, with 50% and 75% Ga sites [Figs. 1(c) and 1(d)]. Results for Figs. 1(a)–1(c) have been discussed earlier in Ref. 5, but for the sake of clarity on the computational details, they are shortly reviewed here.

For the mixed cases, the minimum symmetry possible in the current frame of calculations was used. The plane-wave cutoff energies were 16 and 8 Ry for the nonmixed and mixed geometries, respectively. 24 and 72 special Monkhorst-Pack **k** points in the irreducible Brillouin zone (IBZ), corresponding to 288 points in the full zone, were used to sample the wavefunctions. Regarding the case of 3-ML Si, we used the two alternative structures of the ''segregated'' model [Figs. 2(a) and 2(b)]. Both calculations were performed with a 16-Ry cutoff energy and 21 special Monkhorst-Pack **k** points. The supercells contained three Si layers placed inside nine layers of GaAs.

Each atomic layer within the supercells was assumed to occupy the same volume as in the corresponding bulk. The in-plane Si positions were assumed to be fully adapted to the GaAs lattice. In each case [Figs. 1(a)–1(d), 2(a), and 2(b)] the atomic positions were fully relaxed. The equilibrium geometries were considered as established when all forces were smaller than 0.005 eV/Å, corresponding to an estimated numerical uncertainty of maximum 0.05 Å. To check explicitly that the slab thickness was sufficient in a quantitative way,

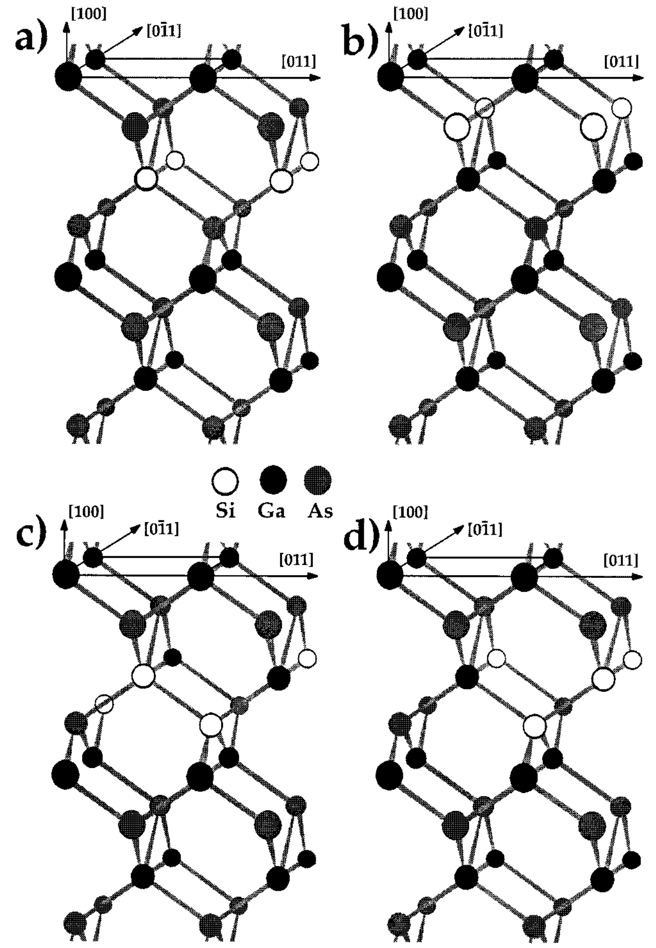

FIG. 1. The atomic geometries used in the calculations for one Si(100) layer. For (a) and (b) it was possible (due to periodicity) to only use one-fourth of the supercell structures (results in Ref. 4), while in (c) and (d) the whole structures were used when calculating the mixed result, thus forcing the use of a lower cutoff.

we investigated the partial density of states (PDOS) and the atomic positions in the central layers. Full agreement with the bulk PDOS was obtained in all cases, and the positions of the central layer ions were found to be within 0.02 Å relative to the ideal ones, despite significant movements in the interface.

We also investigated the influence of the lower cutoff energy in Figs. 1(c) and 1(d) by comparing the PDOS's both for the central layers with those of the other cases, and for bulk GaAs and Si calculated at 8 and 16 Ry, respectively, in each case using six special **k** points in the IBZ. Very good agreement was found for the different cutoffs, thus indicating the validity of the lower cutoff and minimal influence on the SXE spectra. Furthermore, a cutoff energy of 8 Ry has been found by experience to give reliable values for energy differences (and thus forces). This agrees well with the fact that ions also take the ideal position in the central layers in the calculations using an 8-Ry cutoff.

The SXE spectra were calculated within single-particle and dipole approximations according to the approach of Refs. 5 and 17. We should also mention at this point the possibility of additional errors in the explicit heights of the theoretical peaks, and thus in the interpolation scheme below due to the PP DFT-LDA. In principle the PP DFT-LDA may contribute with different errors to the two peaks (due to, e.g., nonlocal effects). To check for such errors, we have compared results from test calculations employing the PP DFT-LDA with those of other computational schemes not relying on these approximations. Bulk fcc Ga PDOS's have been compared with Ref. 18 (Koringa-Kohn-Roslokon muffin-tin LDA) to test the validity of the PP, while the semiconductors have been tested against linear muffin-tin orbital and empirical nonlocal pseudopotential calculations.[19] The agreement for the PDOS of the bulk substances involved is found to be very good. There is nothing that indicates any additional errors in the slab calculations as compared to the bulk cases. Accordingly we believe that any errors induced by the calculational method can be ignored in the present cases.

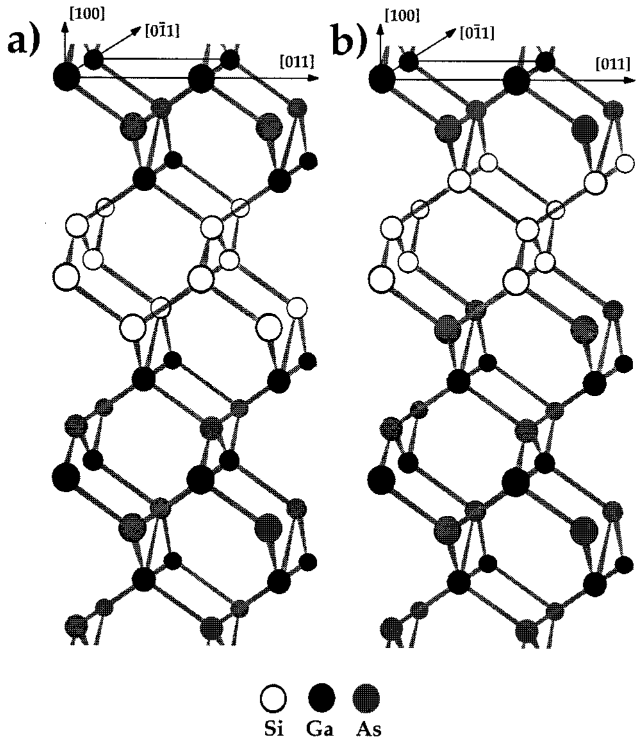

FIG. 2. Geometries used for three Si(100) layers. Due to periodicity it was possible to only use one-fourth of the supercell structures, thus enabling a 16-Ry cutoff.

III. RESULTS—COMPARISON BETWEEN EXPERIMENT AND THEORY

We have earlier[5] tested the calculations by comparing the theoretical Si $L_{2,3}$ SXE spectrum of bulk Si with the experimental one. The experimental spectrum was well reproduced in all features.

The ''segregated'' model returns a good qualitative picture of the physical system.[5] However, it fails to reproduce the SXE spectrum correctly. To improve on the model, we consider arrangements where anion and cation sites are occupied randomly (the ''mixed'' model; see above). Figure 3 shows the corresponding calculated emission spectrum with the Si atoms distributed equally over As and Ga sites (published earlier in Ref. 5) together with the spectrum for 75% of the Si atoms in Ga sites. The separate contributions from the two kinds of sites are also included. All spectra are related to the common valence-band minimum (VBM).

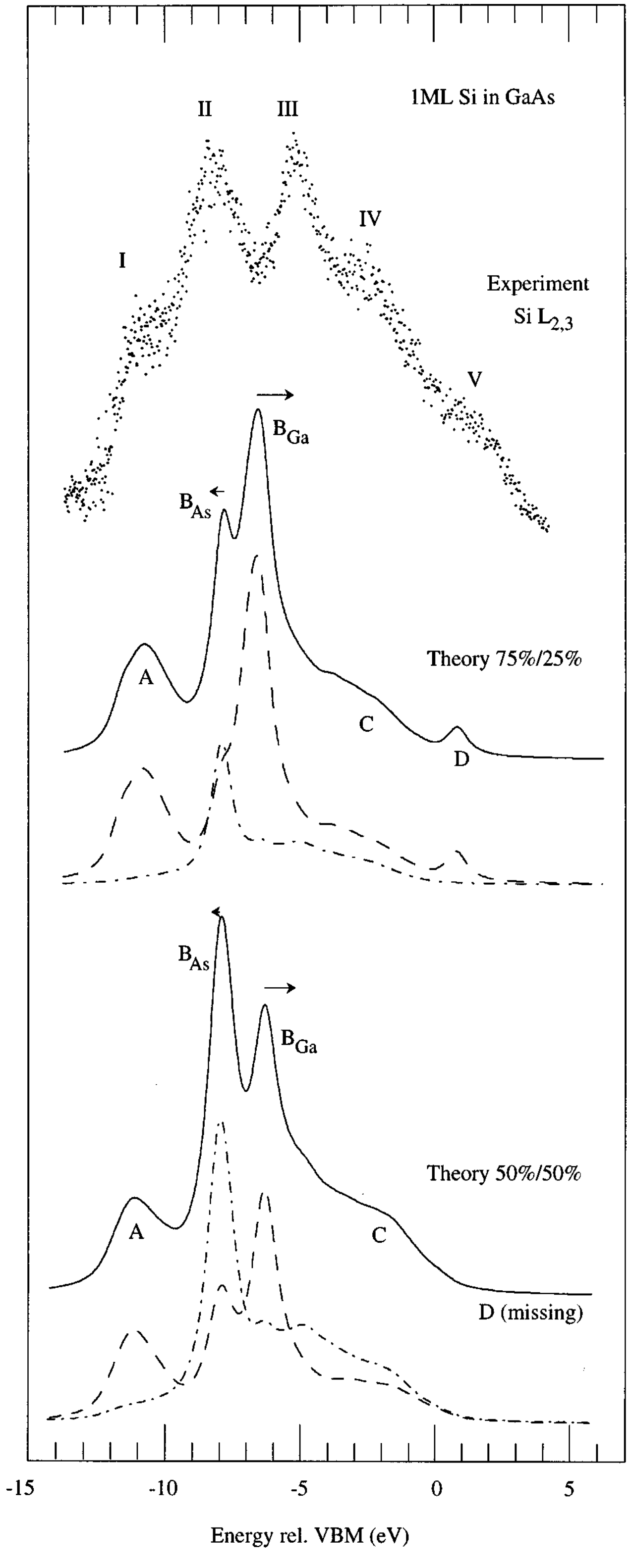

FIG. 3. The experimental SXE spectrum from a Si(100) monolayer in GaAs (dotted), and the theoretical spectra within the ''mixed model.'' The arrows on the theoretical spectrum indicate changes expected due to core-level shifts.

Somewhat unexpectedly, the local PDOS's within this model are qualitatively similar to those found in the ''segregated'' model, with predominantly *s* character in the range of the two major peaks. This may be understood as due to the localized nature of the covalent bonds forming the valence band. We associate the dominant peak (B_{Ga}) for Si atoms in Ga sites in the theoretical spectrum with one of the two strongest experimental peaks (III). The second theoretical peak (associated with peak II) is considerably smaller at this site. This behavior agrees well with that of the Si atoms in well-separated planes.[5] To account fully for the experimental peak II, we also have to consider the ''As-site spectrum.'' The large peak nearly coincides in this case with peak II, and dominates the spectrum as expected from the ''segregated'' model. Regarding the other structures indicated in Figure 3 we find that peak *A* steams from a hybridization with As *s* states, while shoulder *C* is due to *d*-symmetry states. On the whole there remains a pronounced complementary character of the two contributions from different types of sites.

In addition we note a peak *D* above the VBM for the 75–25 % mix, which also seems to be present in the experimental spectrum (structure *V*). Because of its position above the VBM, we associate *D* with emission from Si-induced donor states. There is no counterpart either in the theoretical spectrum for the Si in As sites or any of the spectra in the case of the 50–50 % mix. Investigating the PDOS in detail for the surrounding atoms (Ga and As), we find that these donor states are highly localized in space despite their position well above the VBM. In fact, beyond the nearest neighbors they can hardly be observed at all. We also observe that the Si donor states are positioned 0.32 eV below the GaAs conduction-band minimum (CBM) in the calculation. Thus the donor states will remain localized even at room temperature, the ionization energy being of an order of 10 larger then *kT*. This properly explains how this feature might be seen in the experimental spectrum despite the localized nature of SXE.

There is a clear distribution though, of these states between neighboring Si atoms as opposed to surrounding Ga or As. This motivates the abscence of *D* in the 50–50 % geometry—there is a shortage of electrons in the covalent bonds for Si in As sites that equals the abundance of electrons for Si in Ga sites. Due to local redistribution all doping effects vanish. In the 75–25 % structure the ''compensation doping'' is of course incomplete, thus giving rise to the *D* peak.

When comparing experiment and theory in more detail, we find that the separation between the two main peaks in the calculated mixed spectra is around 1 eV smaller than observed experimentally. The difference is, at least partly, due to the fact that we have not taken into account any core-level shifts. Since the electronegativity of Si is halfway between that of Ga and As, the charge transfer will be in opposite directions for Si in cation and anion sites. Thus the energy separation between the common VBM and the Si $2p$ level should increase/decrease for Si atoms in Ga/As sites, respectively, and the SXE spectra should shift accordingly. The directions of these expected shifts are indicated by arrows in Fig. 3. Assuming that the difference between experiment and theory is due to this effect, the results show that the polarization gives rise to a relative core level shift of ~1 eV. Introducing this shift explicitly in the theoretical spectra would of course improve the agreement between experiment and theory.

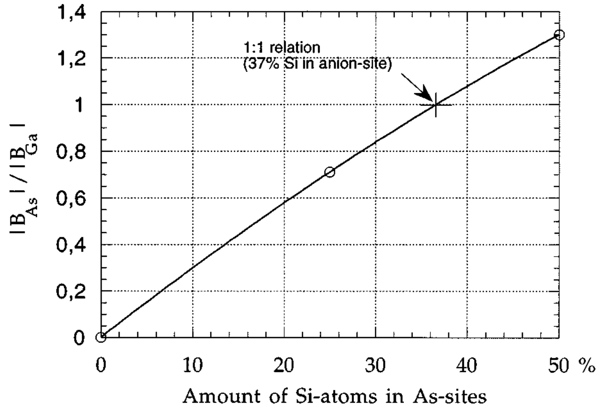

FIG. 4. The ratio between the two main peaks B_{As} and B_{Ga} as extrapolated from the three cases with 0%, 25% and 50% of Si atoms occupying As sites. Experimentally a 1:1 ratio is observed, which can be used to theoretically determine the amount of Si in different sites.

Finally we have used the calculated relative intensities of the B_{As} and B_{Ga} peaks in the three cases of 0%, 25%, and 50% Si in As sites, to establish a relation between the site distribution and the intensities between the two main peaks; see Fig. 4. Since these intensities are of similar magnitude in the experimental spectrum, it is possible to estimate the actual distribution of Si atoms. We find in this way that 63% (±5%) of the Si atoms occupy Ga sites. This kind of distribution indicates that feature *V* should be associated with Si donor states due to excess of Si in cation sites in a similar way to the 75–25 % geometry above. Interpolating the spectra for this mixing (63%) and including the indicated core-level shifts above, we achieve the final spectrum for 1-ML Si in GaAs(100); see Fig. 5. This spectrum agrees extremely well with experimental data. Thus we believe this distribution to accurately describe the embedded Si layer on a microscopic level.

It should be noted, however, that Si in the physical system might redistribute itself over several atomic layers through diffusion during, and possibly after, deposition and the overgrowth of GaAs. However, due to the localized effects we do not believe this to influence the results substantially. The small qualitative changes between the completely segregated model and the mixed ones clearly indicate that the system in large is relatively insensitive to the exact distribution.

Treating the case of 3-ML Si, we only consider the ideal geometries with Si layers in Si_{As}-Si_{Ga}-Si_{As} and Si_{Ga}-Si_{As}-Si_{Ga} planes [Figs. 2(a) and 2(b)]. Given the good qualitative results of 1-ML Si (see Ref. 5) with this simple approach, this ensures at the very least a good understanding of the spectrum. Considering the increased thickness, it is also most likely that the importance of intermixing is considerably less pronounced in the 3-ML case, since in practice only the outer layers might be redistributed. In a first, simple approximation to such a mixing, two out of three layers would still be continuous in the *x*-*y* plane, while the third ML of Si should be redistributed with similar weights above and below this double Si plane. Such an approach would be very numerically costly and possibly improve on details, but clearly the effects should be quite small compared to the 1-ML case. We thus believe that calculations on the ideal geometries should be sufficient to allow for a reliable interpretation of experimental data both in the qualitative and quantitative senses.

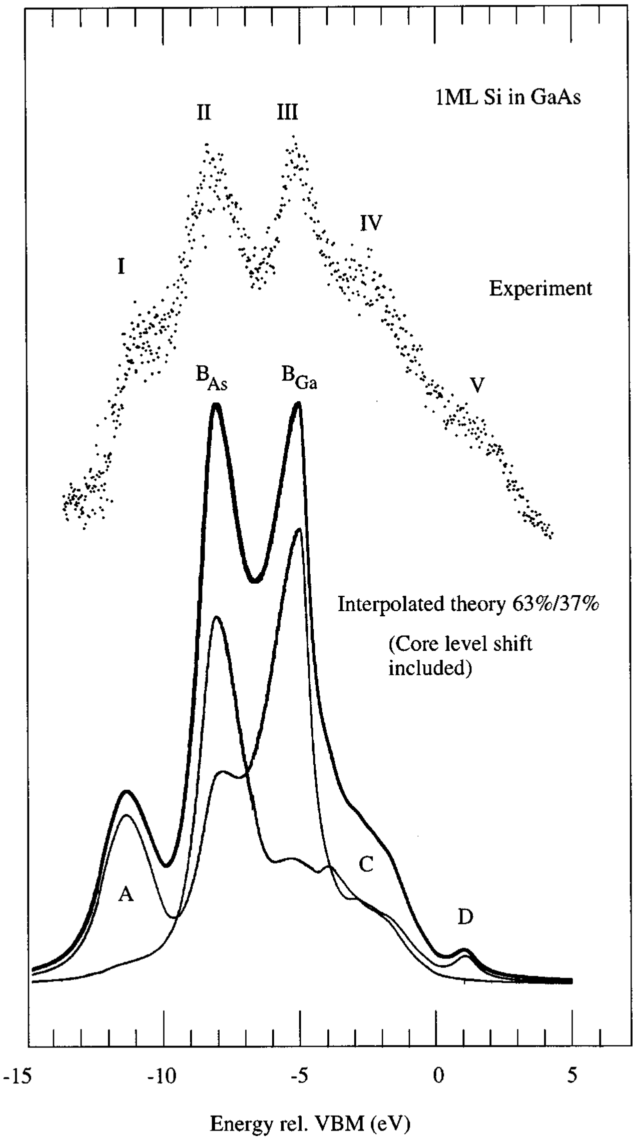

FIG. 5. Interpolated spectrum for the optimal mixing given by Fig. 4. The expected core-level shifts have been included, and the peaks shifted accordingly. Contributions from Si in As and Ga sites are also interpolated and displayed.

In contrast to the 1-ML case, the 3-ML buried Si contains three geometrically different sites. The Si atoms can occupy either cation or anion positions in either of the two outer planes, or they can be positioned at the center of the three-layer Si region. Although this central site might be classified as a Ga or As site, it is more appropriate to consider it as ‘‘pure’’ Si. In a nearest-neighbor approximation, the central Si atom *is* bulk Si. This interpretation is supported by the theoretical spectra and the PDOS of the central layers, which turns out to be rather bulklike. In the case of the Si_{As}-Si_{Ga}-Si_{As} geometric structure [Fig. 2(a)], the agreement of the electronic structure and that of bulk Si (see Ref. 5) is especially good (Fig. 6). A slight shift as compared to the surrounding outer layers results in a broadening of the total spectrum from this geometry.

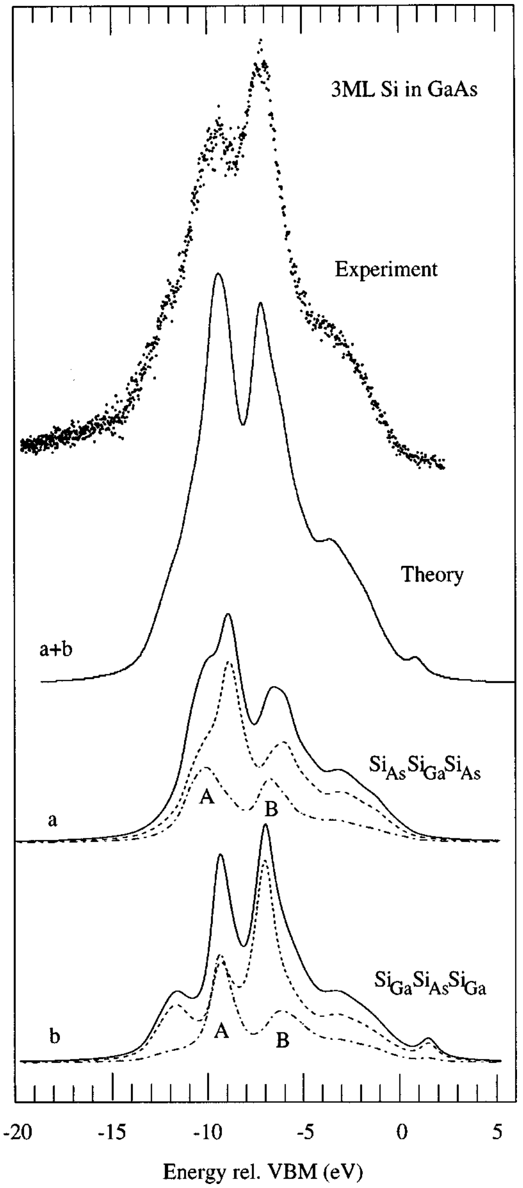

FIG. 6. Calculated spectra from three Si(100) layers with the geometries of Figs. 2(a) and 2(b). The enclosed smaller spectra are the contributions from the central layer (dash-dotted, smallest) and the outer layers (dotted, medium sized), respectively. The total spectrum is also shown.

For the *b* geometry (Si_{Ga}-Si_{As}-Si_{Ga} sites), the differences between the calculated intensities of the central layer and that of bulk Si is considerably larger due to hybridization with the low lying As *s* states on the next-nearest-neighboring As atoms. The reason for the strong influence despite the distance is that the electronic structure of the two outer Si layers in cation positions becomes heavily altered by the As atoms, and thus work as ''pipes'' connecting the central atoms with the As layers. This behavior, we believe, is explained by the fact that Si lacks electrons in the current energy region—i.e., the screening is much less efficient for the low-lying As *s* states as compared to the higher *s* and *p* states of Ga. In the central layer this results partly in a thick tail on the low-energy side, but mainly in the enhancement of the *A* peak. For the outer layers, the familiar low lying *s*-state peak appear below the bulk like features of the central Si atoms.

Regarding the two different outer positions in As and Ga sites (the *a* and *b* geometries), the complementary nature of the spectra remains from the 1-ML case. The differences between the two geometries are, however, much less pronounced, and both types of layers exhibit two dominant peaks instead of a single one. Investigating the character of the PDOS, i.e., the distribution of *s*, *p*, and *d* states together with the physical distribution in real space, we believe the electronic structure to a considerable extent to be bulklike. Thus we give an alternative interpretation of the two peaks in the outer layers as opposed to the 1-ML case. That is, we believe the presence of the two peaks to be partly due to the bulk like part of the PDOS, while the dominating part in each site to arise from hybridization with the surrounding Ga or As atoms. This is very much contrary to the findings for 1 ML, where a mere redistribution of the ''As/Ga-influenced'' PDOS takes place between the Si atoms, and no pure bulk features is to be found. Keeping in mind that these atoms have Si neighbors in three out of four directions, this finding agrees well with simple considerations based on neighbor interactions.

In a similar way to the Ga-site-dominated cases above, we also find a peak well above the VBM in the *b* geometry (Si_{Ga}-Si_{As}-Si_{Ga}) that we associate with Si-induced donor states. These states are, however, positioned just below the CBM and thus not very localized. At finite temperatures, these states should become ionized and the electrons redistributed over the whole volume of the sample. Consequently this feature should not appear in the experimental SXE spectrum at room temperature. Measurements at 0 K might reveal the donor states, but since the outer layers probably mix themselves even further (reducing the surplus of Si in Ga sites, if not eliminating it), the doping effect is likely to be a factor 10 less then in the 1-ML case anyway. In addition the numerical uncertainty is relatively large, $\sim\pm 0.05$ eV, which in reality may put the donor states exactly at, or above the CBM.

Using a straightforward superposition of the spectra from the two three-layer geometries, we obtained the total SXE spectrum (Fig. 6). All main features are well reproduced, with the exception of the Si-induced donor states (see above.) The theoretical spectra show a good agreement with experiment, both in general features and relative intensities. Further investigations including intermixing of the outer layers will probably improve on the heights of the two main peaks, but on the whole the calculations have provided a good picture of the electronic structure of the buried Si layers.

IV. CONCLUSIONS

Ab initio electronic structure calculations have been performed on buried Si(100) layers in GaAs. In the case of one monolayer, the experimental Si $L_{2,3}$ SXE spectrum is well reproduced by the calculations if one assumes a mixed geometry with Si atoms occupying Ga as well as As sites. The calculations indicate a relative shift of the Si 2*p* level between Si atoms in Ga and As sites of ~1 eV, and that 63 (±5)% of all Si atoms occupies Ga sites in the case of

1-ML Si in GaAs. Interpolating the spectra for a 63–37 % distribution of Si atoms in Ga and As sites, respectively, yields excellent agreement with experiments. Spectra for three Si(100) layers have been calculated using two different segregated geometries. The theoretical and experimental spectra show good agreement and the central layer(s) display large similarities with the bulk Si spectrum. Differences as compared to the 1-ML case are found also for the outer layers.

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