Electronic and Atomic Structure of GaAs Epitaxial Overlays on Si(111)

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The atomic structure occurring at the interface between Si(111) and thin GaAs epitaxial overlayers has a pronounced effect on the surface electronic structure, thus making it possible to infer structural information by comparing measured surface-state energies with those calculated for possible interface bonding arrangements. The atomically abrupt interface . . .SiAsGaAs, in addition to being energetically very unfavorable, is inconsistent with measured valence-band photoemission spectroscopy. Our results indicate that the interface is not atomically abrupt.

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The desire to understand the atomic and electronic properties of the GaAs-on-Si interface is driven largely by the technological importance of combining the optoelectronic performance of GaAs with existing Si technology. Although there has been progress recently,[1-4] the detailed atomic structure occurring at the (111) interface between Si and GaAs is still unknown. The Si(111):GaAs thin epitaxial interface has been studied previously by core-level photoemission spectroscopy[1] (CLS) and x-ray standing waves.[2] These studies establish several constraints on the possible interface bonding arrangements. In this Letter we obtain important new information by comparing electronic structures calculated with the first-principles pseudopotential method with angle-resolved photoemission (ARPES) measurements of surface-state energies.

The CLS measurements[1] for Si(111):GaAs establish the presence of a large number of Si atoms with their $2p$ levels shifted by 0.6 eV to higher binding energy. The corresponding core-level shift on the Si(111)1×1:As surface is 0.75 eV. These shifts indicate bonding between Si and As. Although there is no strong evidence in the CLS data for Si—Ga bonding, one cannot infer that there is, in fact, no Si—Ga bonding, because the Ga-induced Si-$2p$ core-level shift may be less than 0.1 eV,[1] and hence undetectable. Si—As bonding causing the 0.6-eV core-level shift could arise from Si residing on nominal Ga sites in the GaAs overlayers or from Si—As bonds at the interface. The x-ray standing-waves measurements[2] were performed on surfaces exhibiting a 1×1 low-energy electron diffraction pattern. They indicate that Ga and As occupy different (111) atomic planes with the Ga atoms located in the lower halves of the (111) double layers and the As atoms located in the upper halves.

Two model 1×1 structures corresponding to low coverages of Ga and As are illustrated in Fig. 1. Each of these has all As atoms in the upper half of the double layers and all Ga atoms in the lower part. Each has a significant number of Si—As bonds. Hence both are consistent with the constraints established by the CLS

and x-ray standing-wave experiments. The . . .SiAsGaAs termination, shown in Fig. 1(a), contains a SiAs double layer embedded underneath a GaAs surface double layer. Consideration of this structure is motivated by the fact that it appears to be a natural consequence of GaAs deposition on the very stable Si(111):As surface shown in Fig. 1(c). The . . .GaAsSiAs termination, shown in Fig. 1(b), contains a GaAs double layer embedded underneath a SiAs surface double layer. Consideration of this structure is motivated by calculations[3] which indicate that it is 0.57 eV per surface atom lower in energy than the . . .SiAsGaAs termination. However, its formation requires that the Si and GaAs intermix during the deposition. These two structures are special cases of the more general structure . . .(Ga_xSi_{1-x})As-(Si_xGa_{1-x})As, where Si and Ga atoms each occupy sites in both the second and fourth layers (from the surface). The . . .SiAsGaAs structure corresponds to $x=0$ and the . . .GaAsSiAs structure corresponds to $x=1$. The calculated[3] total energy of a 2×2 structure with $x=\frac{3}{4}$ is approximately the same as the $x=1$ . . .GaAsSiAs structure. The configurational entropy, S, of a disordered . . .(Ga_xSi_{1-x})As(Si_xGa_{1-x})As structure is

$$S = -2Nk_B[(1-x)\ln(1-x)+x\ln x]$$

and it contributes nearly -0.08 eV per surface atom to the free energy for $x=\frac{3}{4}$ at the substrate growth temperature, $T=580\,°C$. Thus, the free energy $F=E-TS$ is much lower for the interface structures with $x=\frac{3}{4}$ or
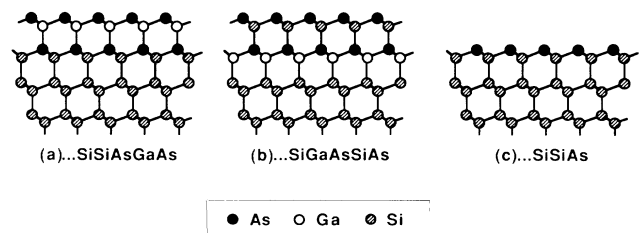

FIG. 1. Schematic views of possible epitaxial Si(111):GaAs overlayer structures, and of Si(111):As.

1 than for the atomically abrupt interface with $x = 0$. It would be remarkable if the high-energy . . .SiAsGaAs termination could in fact be realized as this would imply that the growth process of GaAs on Si(111) is dominated by kinetics over energetics.

The surface electronic structures were calculated with the local-density approximation (LDA) and the first-principles pseudopotential method. The atomic coordinates were obtained by total-energy minimization.[3] The computational procedure is discussed in Ref. 3. For the present electronic-structure calculations we employed a plane-wave cutoff of 10 Ry. The LDA surface states and projected band structures are plotted in Fig. 2(a) for the . . .SiAsGaAs structure, in Fig. 2(b) for the . . .GaAs-SiAs structure, and Fig. 2(c) for the As-terminated Si(111) surface.

The Si(111):As surface has been the subject of extensive analysis,[5-7] and it is well established that the structure corresponds to the As substitutional model shown in Fig. 1(c). The dispersion of the As lone-pair surface states LP in Fig. 2(c), calculated with the LDA, is in reasonably good agreement with experiment.[6] However, a 0.3- to 0.4-eV downward shift of the calculated energy, relative to the valence-band maximum, would be necessary to bring the experimental and theoretical bands into coincidence at the $\bar{K}$ point. The need for this correction arises from the approximate treatment of the self-energy operator in the LDA. Hybertsen and Louie[8] have shown that a full many-body calculation of the surface-state

band structure for Si(111):As results in excellent agreement with experiment. They find that the self-energy correction to the LDA result for the LP state at $\bar{K}$ is -0.25 eV relative to E_{VB} and that the entire conduction band and the antibonding surface state AB are shifted up by 0.6 eV relative to E_{VB}. We believe similar corrections are appropriate for the corresponding states on . . .SiAsGaAs and . . .GaAsSiAs. However, our conclusions do not depend on these self-energy corrections.

For the . . .SiAsGaAs structure there are five surface state bands inside the gap in the [111] projected bulk band structure. These are labeled AB, B_1, B_2, B_3, and LP in Fig. 2(a). B_1, B_2, and B_3 are fully occupied and are localized in the GaAs back-bond region of the surface double layer. These types of back-bond states are also present on the Si(111):As surface, but as resonances in the bulk valence-band continuum. On the . . .SiAs-GaAs surface the back-bond states are shifted into the gap. The reason for this energy shift is the electrostatic dipole which the . . .SiAsGaAs surface has relative to Si(111):As. The dipole is obtained from the different $\Delta V(z)$ between the self-consistent (111) planar average electrostatic potentials $V(z)$ for the two systems. The interface dipole is defined as $\Delta V(\text{vacuum}) - \Delta V(\text{bulk})$. The calculated dipole is 2.6 eV and its sign is such that it raises the energy of surface states relative to bulk Si states. This value corresponds to that obtained[3] with the protonic charge transfer arguments due to Harrison et al.[9] if one assumes a static dielectric constant ≈ 13.
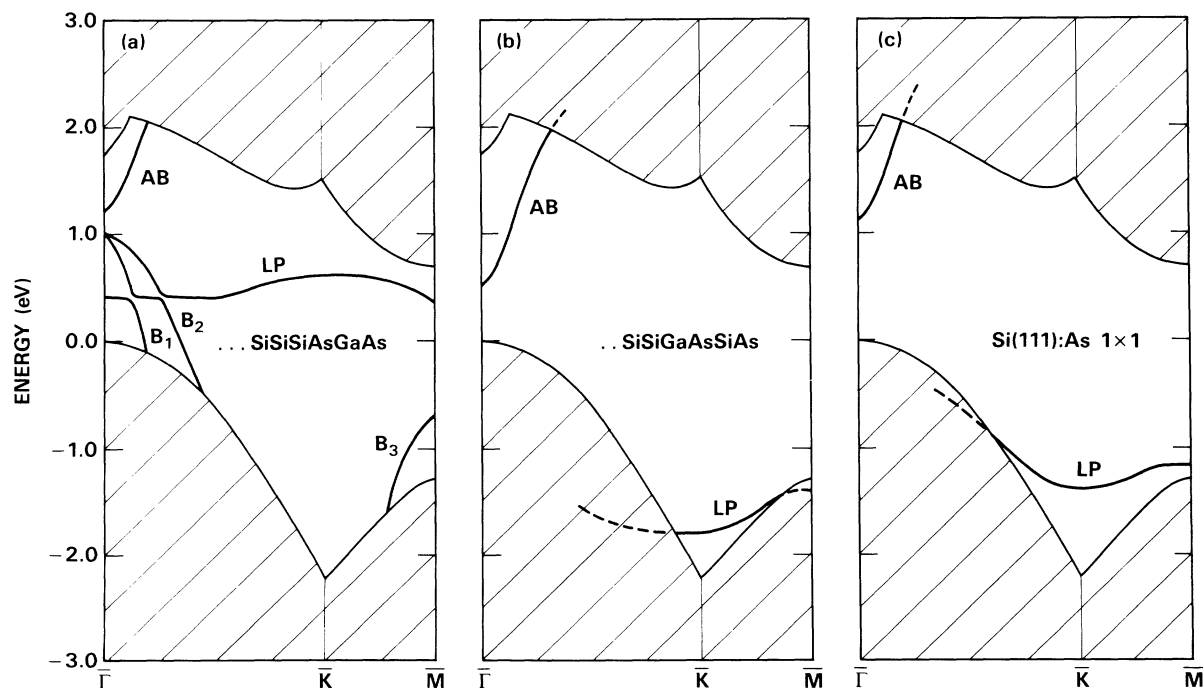

FIG. 2. Calculated surface states (solid lines), and bulk projected band structure (hatched area) for (a) . . .SiAsGaAs, (b) . . .GaAsSiAs, and (c) Si(111):As.

The band labeled LP in Fig. 2(a) corresponds to a lone-pair p_z orbital on the surface As atoms. The lone-pair state also occurs on Si(111):As, but at a much lower energy. The calculated shift is nearly 2 eV at the $\bar{K}$ point, where the LP state is most localized in the surface layer. The band labeled AB in Fig. 2(a) is localized in the antibonding region of the SiAs double layer. On the ...SiAsGaAs surface this double layer is embedded under the GaAs double layer. The AB band also occurs on the Si(111):As surface. It is found at nearly the same energy on the two surfaces because, in each case, it is localized in the SiAs double layer, and this double layer is on the same side of the dipole as the bulk states in the ...SiAsGaAs structure.

The results for the ...GaAsSiAs surface are shown in Fig. 2(b). The lone-pair state, denoted LP in Fig. 2(b), is found to be 1.8 eV below E_{VB} at $\bar{K}$. Thus, at $\bar{K}$ the lone-pair state is 0.4 eV lower in energy on the ...GaAsSiAs surface than on the Si(111):As surface. An antibonding band of surface states, localized in the SiAs double layer, is labeled AB in Fig. 2(b). At the $\bar{\Gamma}$ point AB is shifted downwards in energy relative to its position on the Si(111):As surface by 0.6 eV. For this surface, the energy shifts of the surface states arise from a −0.9-eV dipole. This dipole is $\approx \frac{1}{3}$ as large and of opposite sign compared to ...SiAsGaAs because the protons are transferred by $\frac{1}{3}$ the distance in the opposite direction. The energy shifts of the surface states vary depending on the degree to which they are localized on one side of the dipole.

In general we can expect the energy of the lone-pair state at $\bar{K}$ to shift up or down, relative to its value on the Si(111):As surface, depending on the sign of the interface dipole. According to the proton transfer arguments,[3,9] the interface dipole decreases linearly from 2.6 to −0.9 eV as x increases from 0 to 1. We can therefore obtain interface structural information by comparing the *observed* binding energy of the As lone-pair state on Si(111):GaAs with the *observed* binding energy on Si(111):As.

ARPES measurements were made on thin GaAs layers which were grown on Si(111) substrates using molecular-beam epitaxy methods. At the beginning of GaAs-on-Si(111) epitaxy, the GaAs does not completely cover the substrate and forms islands. The degree of island coverage is of the order of 50%, but depends on details of the growth method.[1] To minimize the difficulty of interpretation of the data, thin GaAs layers were grown with a number of molecular-beam epitaxy methods. The standard molecular-beam epitaxy method of evaporating Ga in the presence of an overpressure of As$_4$ molecules was used to grow films at a nominal growth rate of about 30 Å/min with a variety of deposition times (equivalent to uniform thicknesses of 1, 5, 25, and 50 Å at a substrate temperature of 580°C and 25 Å at 250°C). In addition, GaAs was grown with a Ga-first

method in which a thin Ga layer was evaporated onto the substrate in the absence of any As$_4$ partial pressure and then this layer was annealed in an As$_4$ flux. This procedure decreases the tendency to form islands.[1] The amount of Ga deposited was (i) $\frac{1}{3}$ monolayer, which gave rise to a Si(111):Ga $\sqrt{3} \times \sqrt{3}$ reconstruction (equivalent to a 1-Å GaAs film after reaction with As) and (ii) the same as that deposited in the 5-Å growth with the standard method.

The ARPES measurements were made with unpolarized He I light ($h\nu = 21.2$ eV) at angles corresponding to the $\bar{\Gamma}$ and $\bar{K}$ points of the 1×1 surface Brillouin zone. The photons were incident at 45° from the surface normal. The spectra have been aligned at E_{VB} using a constant value of 0.3 eV for ($E_F - E_{VB}$) for Si(111):GaAs because the bulk Si 2p core-level position was found to remain constant for a large range of GaAs thicknesses. Results are compared in Fig. 3 with those obtained under similar conditions for Si(111):As,[6] GaAs(111) 2×2 (Ref. 10), and GaAs($\bar{1}\bar{1}\bar{1}$) 2×2 (Ref. 10) surfaces. The peak associated with the As lone pair is labeled LP, and the bulk GaAs (Si) peaks are labeled α, β (γ, δ).
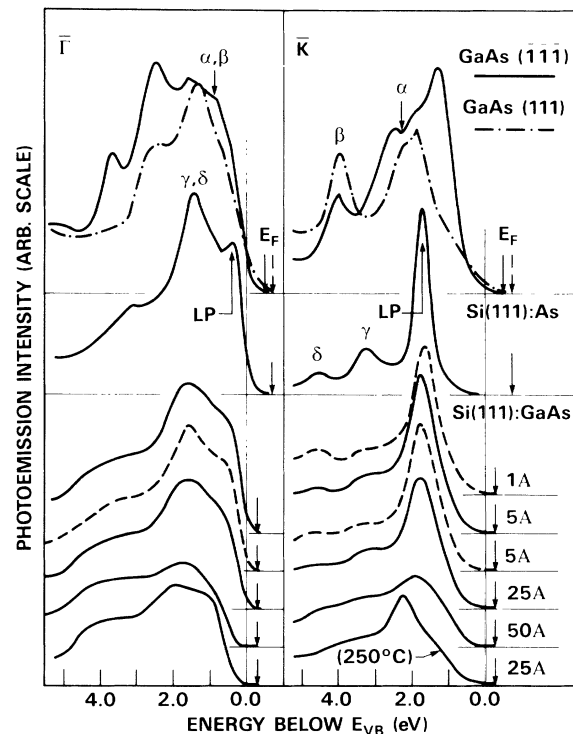

FIG. 3. Angle-resolved photoemission spectra at $h\nu = 21.2$ eV for Si(111):As and for GaAs overlayers on Si(111) and at 20.0 eV for GaAs(111) and GaAs($\bar{1}\bar{1}\bar{1}$). The spectra are taken at emission angles which correspond to the $\bar{\Gamma}$ and $\bar{K}$ points of the surface Brillouin zone. Full lines correspond to layers produced with an As-first growth and broken lines to Ga-first growth. The spectra are aligned at E_{VB} and the position of E_F is indicated by the arrows.

We now compare the surface band structures in Figs. 2(a) and 2(b) with the spectra. The comparison at the $\bar{K}$ point will be emphasized because the difference between the calculated bands is greatest here. The spectra for the $\bar{K}$ point show no states above E_{VB} and no peak until 1.5 eV below E_{VB}. The CLS measurements showed that thick GaAs islands, regions with thin GaAs layers (one or two bilayers) and regions of Si(111):As all coexist on the surface,[1] and the ARPES spectra will contain contributions from all of these regions. The CLS results showed that large regions of thickness corresponding to 1.5-GaAs double layers are present within the deposition variations spanned by the data in Fig. 3. The fact that we see *no* peak at energies above E_{VB} at the $\bar{K}$ point in *any* of the spectra (which correspond to different GaAs equivalent thicknesses and different deposition methods) thus rules out the . . .SiAsGaAs structure. This structure has a LP band above E_{VB} which would give rise to a strong peak in the ARPES spectra for $\bar{K}$. On the other hand, the LP band for the . . .GaAsSiAs structure is expected to give rise to a peak at an energy 0.4 eV lower than that observed on the Si(111):As surface. Experimentally, the surface peak for Si(111):As and the somewhat broader peak for Si(111):GaAs are found to be within 0.2 eV of each other. Therefore it is possible that the Si(111):GaAs peak contains contributions from both . . .GaAsSiAs and Si(111):As regions. The GaAs-on-Si(111) spectra for the $\bar{\Gamma}$ point also show a similarity to that for Si(111):As for the thinner films but the surface peak (labeled LP) washes out as the film thickness increases. For the 25-Å film deposited at 250°C we begin to see the spectrum of bulk GaAs.

In summary, for thin epitaxial GaAs overlayers, the surface state at $\bar{K}$ is observed to have nearly the same energy as observed on Si(111):As. This result indicates that the interface dipole is very small, and rules out the high-dipole (2.6 eV) . . .SiAsGaAs structure because the calculated lone-pair state energy is 2 eV higher than on

the Si(111):As surface. For the . . .GaAsSiAs surface, which has a −0.9-eV dipole, the calculations indicate that the lone-pair state at $\bar{K}$ is 0.4 eV lower in energy than on the Si(111):As surface. This result is in much better agreement with the data. We emphasize that interface structures which have smaller dipoles than . . .GaAsSiAs, and which are equally low in total energy,[3] can be constructed. In fact, the dipole for the structure . . .$(Ga_xSi_{1-x})As(Si_xGa_{1-x})As$ is zero when $x = \frac{3}{4}$. The photoemission results may be indicative of an interface structure of this sort.

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[1]R. D. Bringans, M. A. Olmstead, R. I. G. Uhrberg, and R. Z. Bachrach, Appl. Phys. Lett. **51**, 523 (1987), and Phys. Rev. B **36**, 9569 (1987).

[2]J. R. Patel, P. E. Freeland, M. S. Hybertsen, D. C. Jacobsen, and J. A. Golovchenko, Phys. Rev. Lett. **59**, 2180 (1987).

[3]J. E. Northrup, Phys. Rev. B **37**, 8513 (1988).

[4]M. Zinke-Allmang, L. C. Feldman, and S. Nakahara, Appl. Phys. Lett. **52**, 144 (1987).

[5]M. A. Olmstead, R. D. Bringans, R. I. G. Uhrberg, and R. Z. Bachrach, Phys. Rev. B **34**, 6041 (1986).

[6]R. I. G. Uhrberg, R. D. Bringans, M. A. Olmstead, R. Z. Bachrach, and J. E. Northrup, Phys. Rev. B **35**, 3945 (1987).

[7]R. L. Headrick and W. R. Graham, Phys. Rev. B **37**, 1051 (1988); M. Copel and R. M. Tromp, Phys. Rev. B **37**, 2766 (1988).

[8]M. S. Hybertsen and S. G. Louie, Phys. Rev. B **38**, 4033 (1988).

[9]W. A. Harrison, E. A. Kraut, J. R. Waldrop, and R. W. Grant, Phys. Rev. B **18**, 4402 (1978).

[10]R. D. Bringans and R. Z. Bachrach, Phys. Rev. Lett. **53**, 1954 (1984).