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Atomic structure of one monolayer of GaAs on Si(111)

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Total-energy and force calculations have been performed for thin overlayers of GaAs on a Si(111) substrate. The calculated atomic positions are compared with recent x-ray standing-wave measurements. The atomic positions obtained for the structure in which the stacking sequence is ...SiSiGaAsSiAs are in the best agreement with the x-ray standing-wave measurements. This structure has a significantly lower total energy than the structure ...SiSiSiAsGaAs.

Recently, the atomic structure occurring in the initial stages of epitaxial growth of GaAs on Si(111) substrates has been explored through several kinds of experimental techniques. Bringans *et al.*[1,2] have reported core-level photoemission spectroscopy experiments which probe the type of chemical bonding at the Si-GaAs interface, while Patel *et al.*[3] have reported x-ray standing-wave (XSW) measurements which determine the positions of the Ga and As atoms relative to a periodic array of bulk (111) planes. It was concluded from the photoemission experiments that, in the initial stages, the interfacial bonding occurs predominantly between Si and As. This conclusion is based on the absence of a Si $2p$ core-level shift to lower binding energy which should be present in the case of Si–Ga bonding. The XSW measurements indicated that the Ga atoms occupy sites on the lower half of a (111) doubler layer while As atoms occupy sites on the upper half of the double layer. A structure of this type, shown in Fig. 1, can be formed by addition of a double layer of GaAs to the As terminated Si(111) surface. We will refer to this structure as an AsGaAs termination. The positions inferred from the XSW measurements for these atoms relative to bulk (111) planes are given in Table I. This model is consistent with the conclusions obtained from the core-level data in that no direct Si–Ga bonding occurs.

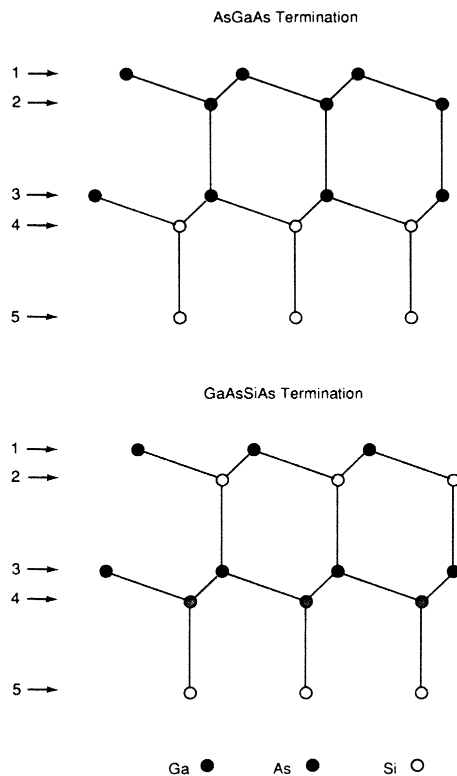

FIG. 1. Side view of projected atom positions in the (110) plane for two possible structures formed by GaAs epitaxy on Si(111). The AsGaAs termination has four Ga–As bonds, three Si–As bonds, zero Si–Ga bonds, and $N+1$ Si–Si bonds in each 1×1 unit cell. The GaAsSiAs termination has three Ga–As bonds, four Si–As bonds, one Si–Ga bonds, and N Si–Si bonds.

In this paper, an alternate structural model consistent with the XSW measurements is suggested. This model is based on first-principles pseudopotential total energy and force calculations which establish the existence of other structures having considerably lower total energies than the AsGaAs termination. It is assumed here that exchange reactions allowing interdiffusion of Si with the arriving Ga and As are not kinetically forbidden. A possible result of such reactions is the GaAsSiAs termination

TABLE I. Comparison of measured Ga and As positions with the calculated positions for two different stacking sequences. The positions, in angstroms, are relative to crystalline Si (111) planes. The measurements are based on the x-ray standing-wave technique (Ref. 3).

Atom	XSW (Å)	Theory (Å)
	AsGaAs termination	
As	0.36	0.26
Ga	0.08	0.41
As	−0.02	0.11
Si		−0.08
Si		−0.03
Si		0.0
	GaAsSiAs termination	
As	0.36	0.27
Si		0.07
As	−0.02	0.10
Ga	0.08	−0.01
Si		−0.02
Si		0.0

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shown in Fig. 1. In this structure, the last four layers are Ga-As-Si-As. The Ga atoms reside in the fourth layer from the surface rather than in the second and Si atoms occupy positions in the second layer. The fifth-layer Si atoms are bonded to three Si and one Ga atom, and the second-layer Si are bonded to four As atoms. Thus, as required by the core-level data, the interfacial Si is bonded predominantly, but not exclusively, to As.

Total-energy and force calculations were carried out for both the AsGaAs and GaAsSiAs terminated surfaces. These calculations employed the local-density formalism[4,5] and the first-principles pseudopotential method.[6] Scalar relativistic norm-conserving pseudopotentials were employed.[7,8] The exchange correlation energy was the parametrized[9] Ceperley-Alder electron gas data.[10] The structures were studied in a centrosymmetric supercell[11] containing six Si atoms, four As, and two Ga atoms. The thickness of the vacuum region is approximately 12.5 a.u. The Kohn-Sham equations were solved in a plane-wave basis containing plane waves with kinetic energies less than or equal to 8 Ry. Forces on the atoms were calculated with the Hellmann-Feynman theorem and used to obtain geometries with successively lower total energies. This type of approach has been employed previously to study chemisorption of Al and As separately on Si surfaces.[12,13]

In Table I, the calculated positions of the layers are given relative to the positions which Si layers would have in a continuation of the bulk structure. The XSW technique measures these relative positions. For the AsGaAs termination, the equilibrium Ga position is very different from that determined by the XSW measurement. The calculation places the Ga 0.41 Å above the second (111) plane while the XSW position is 0.08 Å above this plane. The calculated As atom positions are 0.26 Å (top layer) and 0.11 Å (third layer) and the XSW positions are 0.36 Å (top layer) and −0.02 Å (third layer). While the calculated spacing between the first and second layers, As and Ga, is 0.63 Å, the experimental spacing would be 1.06 Å. The lack of agreement between the calculated and measured Ga position suggests that the AsGaAs termination does not in fact occur.

For the GaAsSiAs termination, the Ga position is predicted to be 0.01 Å below the fourth layer (111) plane. The XSW measurement can be interpreted in terms of Ga atoms positioned 0.08 Å above this plane. In this case, the discrepancy between the calculated and measured Ga position is only 0.09 Å. The calculation places the top layer (As) at 0.27 Å and the third layer (As) at 0.10 Å. The second layer (Si) is calculated to be 0.07 Å above the bulk plane. Consequently, the Si-As first and second interlayer spacing is 0.99 Å. This distance is essentially identical to the interlayer distance (0.97 Å) predicted by total-energy calculations for the As terminated Si(111) surface.[14] Those predictions are in excellent agreement with the XSW measurements by Patel, Golovchenko, Freeland, and Gossmann.[15]

The calculated total energy of the GaAsSiAs termination is found to be 0.57 eV/(surface atom) lower than that for the AsGaAs termination. The convergence of this energy difference with respect to the plane-wave cutoff, E_{pw}, was tested by performing several calculations with E_{pw} ranging between 5 and 8.5 Ry. Over this range, the energy difference changes by less than 0.02 eV, indicating that the energy difference is converged adequately with $E_{pw} = 8$ Ry.

This large energy difference can be understood by consideration of the type of bonds formed in each case. In the AsGaAs structure, one electron must be transferred from the embedded SiAs double layer to the top GaAs double layer to simultaneously form a bond between the double layers and obtain a full As lone pair band. No such charge transfer is required in the GaAsSiAs structure where each double layer already has the proper number of electrons. In the AsGaAs structure, the (longitudinal) As—Ga distance is 2.66 Å; approximately 0.2 Å longer than the As—Ga bond length in bulk GaAs. The increased length of this bond is indicative of weak interaction between the top double layer of GaAs and the As terminated Si(111) substrate.

Both of the stacking sequences discussed above can be analyzed from the point of view of Harrison's theoretical alchemy.[16] Starting from the As terminated Si(111) surface the AsGaAs surface can be constructed (within the pseudopotential framework) by transferring a positive charge from the second to the third layer. The numbering scheme for the layers is given in Fig. 1. This procedure converts the Si into As and Ga atoms and consequently it converts . . .SiSiAs into . . .AsGaAs. The change in the planar average Hartree potential produced by this charge transfer can be estimated by the potential drop between two sheets of positive and negative charge embedded in a dielectric medium. For a static dielectric constant of ∼13 one finds a potential change of ∼2.6 eV for an interplanar spacing of 2.35 Å. This dipole shift tends to raise the energy of the electronic states with most of their weight in the surface double layer relative to bulk Si states. Recalling that the band gap of bulk Si is only 1.17 eV, one might wonder if the large dipole formation could even lead to the partial occupation of the Si conduction band for this geometry. In fact, the local-density-approximation (LDA) calculation shows that the highest-energy occupied surface state is pushed up into the band gap and is nearly degenerate with the Si conduction-band minimum. On the other hand, the GaAsSiAs surface can be formed by charge transfer from the fourth to the third layer of Si(111)1×1:As. In this case, the estimated dipole shift relative to Si(111)1×1:As is about −0.9 eV. The shift is opposite in sign and smaller by a factor of 3 because the charge is transferred through $\frac{1}{3}$ of the distance and in the opposite direction.

Up to now, we have considered only 1×1 symmetry structures where each (111) plane contains a single type of atom. Structures with (111) planes containing both Ga and Si are also possible and might have lower total energies. One possible structure of this type can be formed from the GaAsSiAs 1×1 structure by exchanging $\frac{1}{4}$ monolayer of Ga atoms in the fourth layer with $\frac{1}{4}$ monolayer of Si atoms in the second layer. The structure formed in this way has $\frac{3}{4}$ monolayer of Ga and $\frac{1}{4}$ monolayer of Si in the fourth layer, a full monolayer of As in the third layer, $\frac{1}{4}$ monolayer of Ga and $\frac{3}{4}$ monolayer of

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Si in the second layer, and a full monolayer of As in the surface layer. This structure has no dipole in the sense discussed above. Total-energy calculations were carried out for this structure. Because a 2×2 unit cell with 48 atoms is necessary in this case, the plane-wave cutoff was limited to 5 Ry and the atomic coordinates were not fully optimized. The total-energy difference between this structure and the 1×1 GaAsSiAs structure is found to be very small. The energy difference is of order 0.01 eV/(2×2 cell). This suggests that (111) planes of mixed atomic types are possible in the initial stages of GaAs epitaxy on Si(111).

In summary, it is proposed that during the initial stages of GaAs deposition on Si(111), exothermic reactions intermix Si with the arriving Ga and As to form a structure in which the stacking sequence is predominantly . . .SiSi-GaAsSiAs. This structure is consistent with recent x-ray standing-wave measurements and core-level photoemission data.

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