Structural compromise of the arsenic-terminated silicon (111) surface

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The generalized-valence-bond method of electronic-structure calculation has been used to calculate equilibrium bond angles and bond lengths in a cluster representing the ideal Si(111)-(1×1)As surface. These are compared to equivalent parameters for the trisilylarsine molecule [(SiH$_3$)$_3$As]. This molecule is assumed to represent an "ideal" structure for the Si$_3$As unit since the Si atoms are not constrained to specific lattice positions. Nearest-neighbor distances between Si atoms in a Si(111) plane are 0.4 Å greater than the distance found in trisilylarsine. The structure of the Si(111)-(1×1)As surface can then be regarded as resulting from a compromise between "ideal" Si—As bond lengths and bond angles, given the constraints of the (111) surface atomic positions.

The Si(111)-(1×1)As surface was initially studied by Olmstead *et al.*[1] and Uhrberg *et al.*[2] who employed core-level spectroscopies and low-energy electron diffraction (LEED)[1] and angle-resolved photoemission and total-energy pseudopotential calculations[2] to show that As atoms replace the outermost Si atoms in a "bulk-terminated" Si(111) surface resulting in a stable, passivated surface. More recently, medium-energy ion scattering (MEIS),[3,4] x-ray standing wave (XSW)[5] and scanning tunneling microscopy (STM)[6] have been used to study this surface and structural parameters have been obtained.

This surface has a phenomenological interest since it resembles a Si(111)-(1×1) surface in which each dangling-bond orbital is doubly occupied instead of being singly occupied as would be the case in the Si(111)-(1×1) surface. Thus the inherent instability of an ideal Si(111)-(1×1) surface is removed because the unpaired electrons of that surface are now coupled into a stable lone pair when the top layer of Si is replaced by As.

Here we report the results of generalized-valence-bond (GVB) calculations on a cluster representing this system and structural parameters derived from minimization of the total energy of the cluster as a function of As-atom location. These parameters are compared to those derived from experiment[3–5] and theory[2] and those of the trisilylarsine molecule [(SiH$_3$)$_3$As], and it is found that the GVB results compare closely to experiment and a previous calculation but all differ significantly from the trisilylarsine parameters. The reason for this finds its root in the valence of atomic As and is reflected in the orbital plots for the cluster used to model the surface in this work.

To date, experimental and theoretical studies have modeled the surface in terms of a parameter (R, say) which is the displacement of the As atom in the z direction from the position of an Si atom in the first layer of an unreconstructed surface. This single parameter is sufficient to describe the structure of the model surface because the As atom occupies the symmetric threefold site above the three second-layer Si atoms, however, in order to understand the structure adopted in the Si(111) surface, it is more helpful to describe the Si$_3$As unit in terms of the Si—As bond length *and* the Si—As—Si bond angle.

TABLE I. Silicon-arsenic bond lengths and silicon-arsenic-silicon bond angles in trisilylarsine and the arsenic terminated silicon (111) surface.

System	R_e Si—As (Å)	∠Si—As—Si (deg)	R (Å)	Method
(SiH$_3$)$_3$As	2.355±0.001	93.79±0.17		electron diffraction[a]
Si(111)/As	2.45	103.2	0.25	GVB (this work)
Si(111)/As	2.42	105.0	0.19	LDF calculation[b]
Si(111)/As	2.44±0.03	103.7±1.6	0.24±0.06	MEIS expt.[c]
Si(111)/As	2.42±0.04	105.0±2.5	0.2±0.1	MEIS expt.[d]
Si(111)/As	2.41±0.1(5)	105.5±0.8	0.17±0.03	XSW expt.[e]

[a]Reference 7.
[b]Reference 2.
[c]Reference 3.
[d]Reference 4.
[e]Reference 5.

We make the assumption that the Si—Si and Si—As distances are relaxed in the trisilylarsine molecule [because it is free of the constraints on Si—Si distances in the Si(111) surface] and are *transferable* to the solid surface so that the geometry of Si$_3$As in the molecule represents an "ideal" structure for these atoms bonded in an approximately tetrahedral environment. The Si—Si distance in a (111) plane of Si is 3.84 Å, which is significantly larger than the Si—Si distance in trisilylarsine (3.44 Å).[7] Therefore it is obvious that As bonded to three silicons in the (111) plane cannot attain the bond lengths and bond angles of trisilylarsine because of the larger separation of Si atoms in the Si(111) plane compared to trisilylarsine; in the surface the bond angles and bond lengths are expected to be larger and longer. Bond angles and bond lengths are compared in Table I for the Si(111)/As surface and the trisilylarsine molecule (the value of the R parameter is included for reference purposes). The equilibrium Si-As bond length and bond angle determined in our calculations were 2.45 Å and 103.2°, respectively.

From the bond-length and bond-angle parameters in Table I it is obvious that the Si—As bond length and bond angle of the Si(111)/As surface are, respectively, longer and greater than those of the trisilylarsine molecule, and that experiment and theory agree well on the structural parameters—although this is not so evident when the R parameters are compared.

We interpret these data as follows: In molecules where As is covalently bonded to three atoms (such as trisilylarsine) it prefers to adopt an electronic configuration in which the lone pair is predominantly of s character and the covalent bonds are of p character resulting in bond angles about the As atom close to 90°. This is a result of the relatively large s-p energy separation in the As atom which reduces hybridization between s and p functions and which largely overcomes the increased bond-pair–bond-pair repulsion when the tetrahedral angle collapses towards 90°. However, when this is carried over to the Si(111) surface we find that the Si—As bond would have to be extraordinarily long to achieve a bond angle near 90° because the Si positions are constrained to be much further apart in the solid than in the trisilylarsine molecule. Instead a compromise results and a longer bond is formed than in the molecule and the bond angle found in trisilylarsine of around 94° opens up to around 104° in the Si(111)-(1×1)As surface.

The orbital picture which is derived from our GVB calculations is shown in Fig. 1. In this wave function each orbital is singly occupied and a chemical bond or lone pair is described by the overlap of two such inequivalent orbitals. The orbitals shown in Fig. 1 belong to the Si—As bond and the As lone pair. The nature of the orbitals can be seen in their shape—the As lone pair is largely of s character, the Si—As bond consists of an orbital mainly localized on the Si atom which is of approximately sp^3 character and an orbital mainly localized on the As atom which has considerably more p character. The tendency of the As atom to prefer to form three covalent bonds at 90° with respect to each other is reflected in the fact that there is more amplitude in the Si—As bond orbital *below* the bond axis than above—the Si—As bonds are bent inwards slightly.

DETAILS OF CALCULATIONS

As stated above, our model consists of a Si$_3$As unit. This is terminated by nine specially modified H atoms[8]
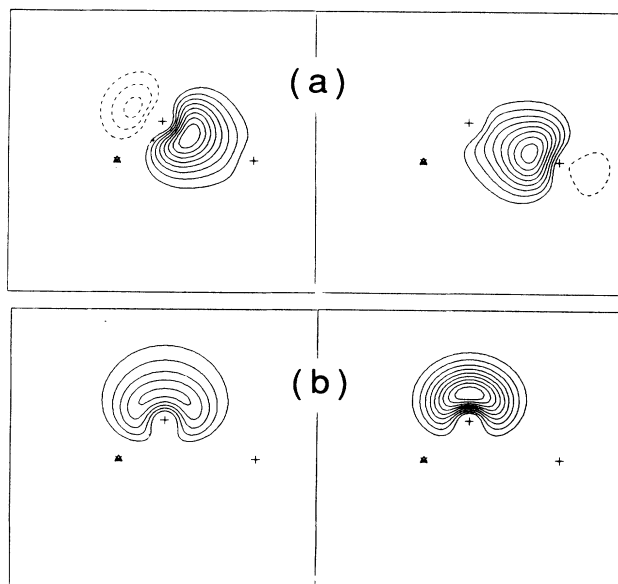

FIG. 1. Orbitals representing (a) one of the three equivalent Si—As bonds between atoms in the first and second layers and (b) the As lone pair. In-plane atomic positions are marked by crosses, out-of-plane atoms are indicated by X's and triangles. Atomic positions of H^x terminating atoms are not marked although they were located in the directions of the bulk Si—Si bonds at a Si—H^x appropriate for the terminator atoms (Ref. 10).
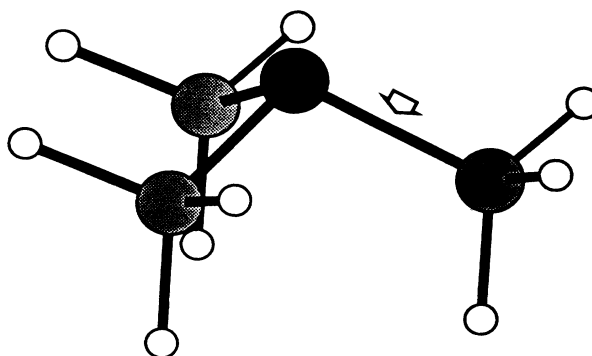

FIG. 2. (SiH$^x_3$)$_3$As cluster model. Solid circle, As; shaded circle, Si; unshaded circle, H^x. The silicon-arsenic bond whose orbital representation is shown in Fig. 1(a) is indicated by an arrow.

(denoted H^x) which have been optimized to preserve charge neutrality in the terminating Si—H^x bond. The geometry of the Si(111) surface requires that the model cluster have the molecular formula $(SiH^x_3)_3As$ with terminating atoms placed in the directions of the nearest-neighbor Si atoms. The geometry of the cluster is shown in Fig. 2. In this work the GVB programs[9] employed the strong orthogonality and perfect pairing approximations to the GVB scheme throughout. Effective core potentials (ECP)[10] were employed for Si and As atoms. Only the valence shell of each atom was treated explicitly using the

double-ζ-plus-polarization basis sets designed for these ECP's.[10] Polarization functions are important in arriving at accurate Si—As bond lengths and angles; in the absence of polarization functions the calculated equilibrium bond length and bond angles were 2.50 Å and 100°, respectively.

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