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LETTER TO THE EDITOR

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Abstract. The electronic structure of the arsenic terminated silicon (100) surface is calculated using the tight binding method in the extended Huckel approximation. The results are compared with the reconstructed silicon (100) surface, and the passivation of the silicon surface is discussed in context of our results.

Amorphous As capping has been used as a convenient method to protect clean Si substrates and has often been employed where the substrates are to be transported between laboratories. Thermal decapping in ultra-high vacuum results in an ordered As monolayer remaining on the Si(100) surface. Such As terminated Si surfaces are very stable. There is hardly any detectable oxidation even when such surfaces are exposed to air for a brief period. This passivation of the silicon surface is highly desirable in many applications. It is therefore important to achieve a good understanding of the passivation process, especially as it might be extended to other systems. Uhrberg *et al* [1] were the first to make a detailed study of the Si(100)–As 2×1 system. They performed an angle-resolved photoemission spectroscopy experiment and their data were subsequently compared with the results of an *ab initio* pseudopotential calculation. Good agreement was found and their results suggested that the As atoms form symmetric dimers with 2×1 symmetry. Further, energy minimization of the structure enabled them to estimate the As–As dimer bond length and the As–Si back bond length. X-ray standing-wave measurements of the distance of the As dimers normal to the ideal (100) surface were found to be in agreement with the calculated distances [2]. Comparison of the calculated and experimental electron band dispersion allowed Uhrberg *et al* [1] to identify the existence of surface states due to the As overlayer. Calculation and experiment were deemed to be in good agreement and the passivation was attributed to the filling up of both bonding (π) and antibonding (π^*) combinations of the dangling hybrids of the As atoms. The calculations also predicted a very small energy separation between these states consistent with the single observed peak in the [001] spectra. However, there is discrepancy in that the calculated energies needed to be rigidly shifted by 0.75 eV to match the experimental results. This was explained in terms of the differences in the self-energy corrections for surface and bulk states. Such discrepancies arise in calculations using density functional theory [3]. In this letter we report on the results of self-consistent calculations using the tight binding method in the extended Huckel approximation (TBEHT).

Table 1. Values of the parameters used in the calculation. The meanings of the various symbols are given in reference [6].

	Si	As
η_s	1.90	3.13
η_p	1.41	1.89
C_s	14.95	17.58
C_p	7.77	11.16
B_s	12.39	12.10
B_p	10.13	10.22
K_{ss}	1.75	1.28
K_{pp}	1.75	6.33
$K_{\alpha\beta}$	1.46	1.98

When performing calculations of surface or interface structures, because of the inequivalence of the atoms, it is important to take account of charge transfer between the interface (surface) atoms and those in the bulk region. It is therefore essential that the calculational scheme that is employed is able to do this. *Ab-initio* techniques, like, for example, the pseudopotential method, allow the charge to redistribute until it is consistent with the total potential of the system. However, for reasons alluded to above, such approaches based on density functional theory give incomplete descriptions when surfaces or metal–semiconductor interfaces are considered. The TBEHT method on the other hand does not suffer from this shortcoming. For example, the parameters are designed to reproduce the experimental band gap in silicon. The Si(111) surface states are correctly predicted. Further, we have shown that this method gives the correct Schottky barrier heights (SBH) at silicide–silicon interfaces [4]. Even the calculated pressure dependence of the SBH is in remarkable agreement with experiment [5]. Hence, this approach is ideal for the study of the Si–As system.

In the TBEHT, the basis functions are taken to be Slater orbitals of single or double zeta functions [6]. The overlap matrix elements $S_{ij}^{\alpha\beta}$ of the atomic orbitals α and β centred on atoms i and j are evaluated explicitly, whilst the Hamiltonian matrix is constructed in the following way. $H_{ii}^{\alpha\alpha}$ is taken to be the negative of the orbital ionization potential I_i^α, and the off-diagonal elements are given by

$$H_{ij}^{\alpha\beta} = K_{\alpha\beta} \left(\frac{I_i^\alpha + I_j^\beta}{2} \right) S_{ij}^{\alpha\beta}. \qquad (1)$$

The constants $K_{\alpha\beta}$ and the exponents of the Slater orbitals, η_α, were adjusted to reproduce the bulk band structures of Si and As. The ionization potentials were made to depend on the excess charge, δq_i, at each site

$$I_i^\alpha = C_\alpha + \delta q_i B_\alpha \qquad (2)$$

with the values of B and C derived from atomic spectroscopic data. The optimized parameters are listed in table 1.

Calculations were performed on the Si(100)–As 2×1 system and for comparison also on the Si(100) 2×1 structures. For both these structures, the surface was modelled by a periodic slab consisting of 14 atomic layers, each comprising of two atoms. The only difference between the two calculations was that in one case the Si dimers were replaced by As dimers. The bond lengths were also different. For the Si surface, the atomic
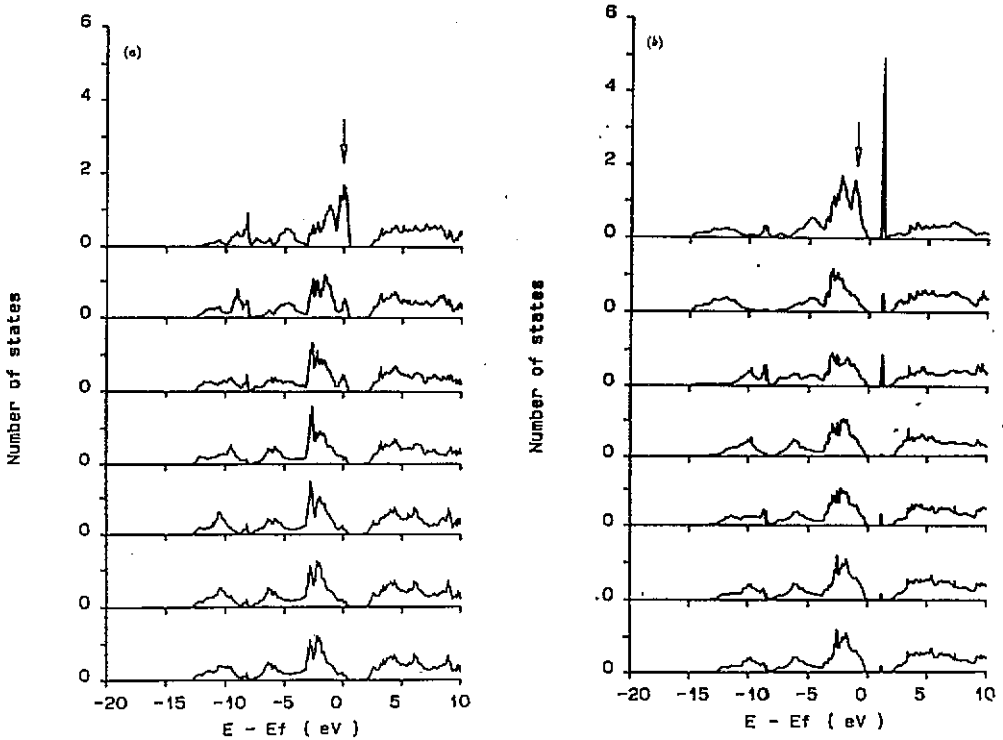
Figure 1. LDOS for (*a*) the Si(100) 2 × 1 and (*b*) the Si(100)–As 2 × 1 structures. The surface layer is shown on top with the six layers below it. The surface state just below E_F is marked by the arrow.

positions were taken to be those reported by Abraham and Batra [7], and for the As terminated surface, the results of Uhrberg *et al* [1] were utilized. At each step of the calculation, the charge on each atom was evaluated and the ionization potential altered in accordance with equation (2). The procedure was continued until self-consistency in the charge on each site was achieved. Finally, the density of states was calculated using the tetrahedron method.

The local density of states (LDOS), layer by layer for half the slab is shown in figure 1(*a*). The central layers are clearly those of bulk silicon. Surface features begin to show in the second silicon layer below the surface. A comparison of the LDOS of the As layer with that of the first silicon layer below the surface, shows the existence of two highly localized features near the Fermi level, E_F. There is a state 1.25 eV below E_F with a width of about 1.0 eV and a highly non-dispersive state 0.83 eV above E_F. The latter state can hold one electron per As atom. The large gap between the occupied and unoccupied states is clearly the reason for the passivation of the surface. This is even more obvious when comparing these results with those of the Si(100) 2 × 1 reconstructed surface. The LDOS displayed in figure 1(*b*) shows a double state at E_F which is only partially filled, and is therefore readily available for bonding to oxygen. It should be noted that this calculation is for the symmetric dimer model and not the generally assumed asymmetric dimer configuration. The purpose of this calculation was simply to highlight the effect of the extra electron on the As atom. It would appear that the double
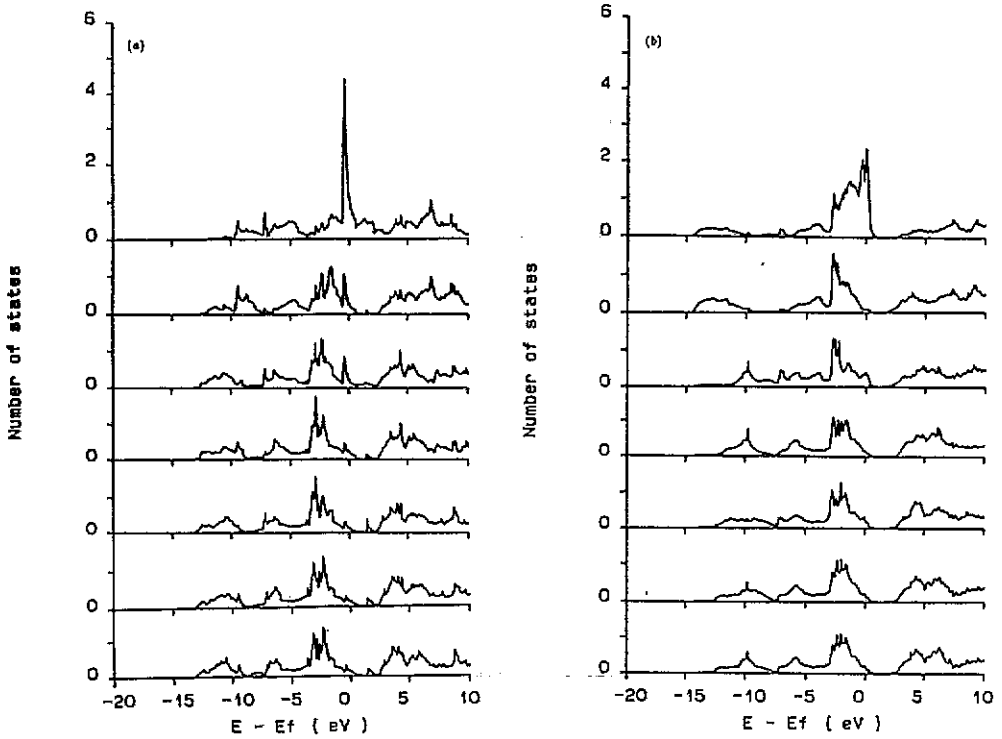
Figure 2. LDOS for (*a*) the Si(100) 1 × 1 and (*b*) the Si(100)–As 1 × 1 surface structures.

state for the Si surface is now split into a filled state and an empty state suggesting that the two extra electrons on the As atom fill up one hybrid bonding state. For further comparison, we have also performed calculations on the Si(100) 1 × 1 and Si(100)–As 1 × 1 unreconstructed surfaces. From the results displayed in figure 2, it can be observed that non-dimerization results in unhybridised states at E_F where there is peak in the DOS.

The results of our calculation are in excellent agreement with the photoemission result of Uhrberg *et al* [1], in that the surface state is at the right energy below the valence band maximum and the width compares favourably with the observed spectra. We have also shown that the passivation of the Su surface is due to the splitting of the state at E_F into a completely filled bonding state and an antibonding state about 1 eV above E_F.

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