Electronic structure of the arsenic-passivated Si(111) surface

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An empirical tight-binding (ETB) approach combined with a Green's-function (GF) method has been employed to investigate the electronic structure of the Si(111) and arsenic-passivated Si(111) surfaces. An accurate silicon band structure has first been developed keeping up to second-nearest-neighbor terms in the Hamiltonian. The ETB-GF approach has allowed the calculation of the local density of states (LDOS) at various atomic layers of the semi-infinite samples. It has also been possible to calculate the contribution of the individual atomic orbitals to the LDOS. The results obtained for the arsenic-passivated Si surface provide the position and strength of localized surface states as well as the density of the bulk states in the valence band, the band gap, and the conduction band. The calculated localized states reproduce the existing experimental data and other partial calculations. Furthermore, this calculation predicts a localized state in the conduction band, which has so far not been studied experimentally.

I. INTRODUCTION

Over the last two decades, a great deal of attention has been focused on the electronic structure of Si and Ge surfaces, mainly because of their importance in the construction of modern electronic devices. The Si(111) surface created either by cleaving or sputtering is known to have 2×1 or 7×7 reconstructions, respectively. It has been found that the surface reconstruction of Si(111) can be eliminated by exposing it to arsenic, which replaces the outermost atoms of the Si surface double layer by As atoms, and the resulting surface structure is very close to the ideal unreconstructed (1×1) surface.[1–4]

In this paper we have used the Green's-function (GF) method[5] to study the electronic structure of the As-passivated (111) surface of a semi-infinite Si sample. In conjunction with the semiempirical tight-binding scheme,[6] the GF method provides an efficient avenue to obtain reasonably accurate numerical results not only for solid surfaces, but also for more complicated cases, such as interfacial systems, adsorption on surfaces, etc. In this formulation the Dyson equation is utilized to calculate the GF of a complex system in terms of those of simpler components. One of the advantages of this method is that it permits the calculation of the density of states (DOS), both extended (bulk) and localized (surface), at any arbitrary layer of the solid, and, if desired, the contributions from particular orbitals (s,p, etc.). The GF method yields the energy location and the strength of the surface states, as well as the way they decay into the bulk.

In this work, we first generate an empirical tight-binding (ETB) Hamiltonian for silicon which gives an accurate description of its band structure. Then using the GF-Dyson equation method for this Hamiltonian we study the DOS at the Si surface layer, and at the $\bar{\Gamma}$ point of the surface Brillouin zone (SBZ) with particular emphasis on the surface states. We next calculate the local density of states (LDOS) of the more realistic unreconstructed (1×1) As-passivated Si(111) surface, and show that our results reproduce all available experimental surface states and are in basic agreement with several theoretical results which individually show only some of these surface states. We also predict a surface state in the conduction band which has so far not been studied either experimentally or theoretically.

II. MODEL

As a starting point, we consider a tight-binding (TB) Hamiltonian similar to that of Chadi and Cohen (CC) (Ref. 7) for the bulk bands of silicon. Silicon possesses diamond structure, so that each atom is tetrahedrally coordinated and each primitive cell contains two Si atoms ($\nu=1$ and 2), connected by the vector $\mathbf{t}=a(1,1,1)/4$, where a is the lattice constant. Hence two Bloch functions can be constructed for each basis function (on the Si atoms), of which there are four (s, p_x, p_y, and p_z) per atom in the CC model. In terms of Bloch functions then, the Hamiltonian $H(\mathbf{k})$ is block-diagonalized into 8×8 blocks, so that, for each $\mathbf{k}$ value, there is a corresponding 8×8 secular determinant to be solved, in order to obtain the energy eigenvalues $E(\mathbf{k})$. It is then straightforward[8] to construct the bulk GF $G(E,n,n',\mathbf{k}_\parallel)$ in the mixed Wannier-Bloch representation, where the wave functions are given by $|n,\mathbf{k}_\parallel\rangle$, n being the index representing the layer number, and $\mathbf{k}_\parallel$ the wave vector parallel to the surface, from which the bulk DOS is calculated as

$$\rho_b=-\frac{1}{\pi}\mathrm{Im}\,\mathrm{Tr}\sum_{k_\parallel}G(E,n,n',k_\parallel)\ . \tag{1}$$

In the CC model, seven parameters were used to obtain a good fit to the valence bands of Si, as calculated by the empirical pseudopotential method (EPM).[9] However, the model gave a poor fit in the conduction band. In this paper, we use nine parameters which give a much better fit to the lower conduction bands. The additional two parameters used here represent second-nearest-neighbor interactions for the diagonal $3s$ and $3p$ matrix elements.

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Two other parameters representing second-nearest-neighbor interactions for the off-diagonal $3s$ and $3p$ matrix elements were also considered. The improvement of the band structure by adding the latter two parameters was only slight and, for the sake of simplicity, they are not used in the present calculations. The resultant band structure and numerical values of the parameters (in Slater-Koster[6] notation) used are shown in Fig. 1 and Table I, respectively. The eigenvalues obtained here are in good agreement with the EPM calculations. For comparison, in Table II we show the eigenvalues obtained in this analysis along with the results of the EPM and other TB calculations. The top of the valence band is chosen at 0 eV and the bottom of the conduction band is found to occur at 3.43 eV. This is consistent with Harrison[10] who shows a band gap of 3.4 eV at the Γ point. Note that the experimental indirect band gap of ~ 1.1 eV between the Γ and X points is maintained in our calculation. However, the differences in the eigenvalues between the EPM and TB calculations result in corresponding differences of the band edges. Of particular interest is the bottom of the conduction band (2.23 vs 1.60 eV) and the bottom of the first valence band (-1.23 vs -1.79 eV) at the L point. They are used to aid in making comparison with presently available experimental and theoretical data. Figure 2 shows the LDOS of bulk silicon (111) at the $\bar{\Gamma}$ point of the Brillouin zone for the energy range of -13 to $+8$ eV. The contributions of the s and p orbitals are shown by the dotted and the dot-dashed curves, respectively. It should be mentioned that, in this and subsequent figures, due to the complex nature of the computations, some extraneous oscillations in the density of states occurred in areas where there is an overlap of several bands. The calculations were done in several different ways, and although the oscillations persisted, their nature varied leading to the conclusion that they are an artifact of numerical approximations. Therefore, in those areas the curves were smoothed to eliminate the extraneous oscillations.

In order to compute the surface GF, g, for the (111) surface of Si, we adopt the Dyson equation approach, wherein g is related to the bulk GF, G, by[5]

$$g = G + GVg \;, \tag{2}$$

where the scattering potential V is

$$V = h - H \;, \tag{3}$$

with H (h) the corresponding Hamiltonian for the bulk (semi-infinite) system. While the model, in its present

TABLE I. Tight-binding parameters for Si and As [using the notation of Ref. 6, and (000) data from Ref. 10].

	Parameter	Value[a] (eV)	
For silicon:	$E_{ss}(000)$	0.0	
	$E_{ss}(110)$	0.0945	
	$E_{xx}(000)$	7.03	
	$E_{xx}(011)$	-0.375	
	$E_{xx}(110)$	0.181	
	$E_{ss}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	-2.0575	
	$E_{sx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	1.00	
	$E_{xx}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	0.428 75	
	$E_{xy}(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	1.35	
For the As outer layer:	$\Delta E_{ss}(000)$	-3.78	(δ_s)
	$\Delta E_{xx}(000)$	-2.46	(δ_p)

[a]These values are within the range of values given in Refs. 10 and 14.

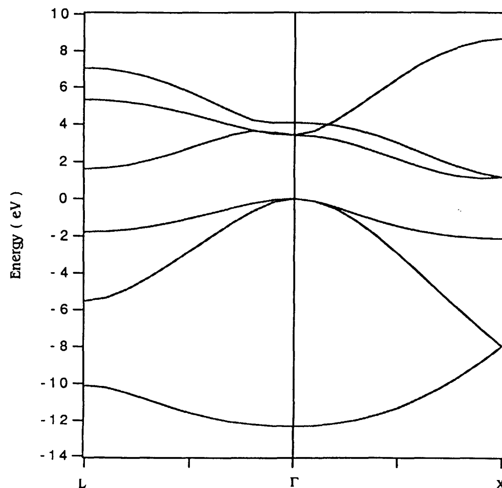

FIG. 1. Silicon band structure calculated by using the empirical tight-binding Hamiltonian developed in this paper. Note that this band structure has a much better agreement in the conduction band with the pseudopotential calculation than that of CC.

TABLE II. Comparison of eigenvalues in eV at three points in the Brillouin zone.

Location	Chelikowsky and Cohen (EPM)	This paper (ETB)	Chadi and Cohen (ETB)
Γ	-12.36	-12.36	-12.26
	0.0	0.0	0.0
	3.43	3.43	3.42
	4.1	4.1	4.1
X	-7.69	-7.99	-7.7
	-2.86	-2.13	-2.88
	1.17	1.17	5.38
		8.7	12.14
L	-9.55	-10.12	-9.44
	-6.96	-5.52	-7.11
	-1.23	-1.79	-1.44
	2.23	1.6	3.2
	4.34	5.33	7.6
		7.04	10.2

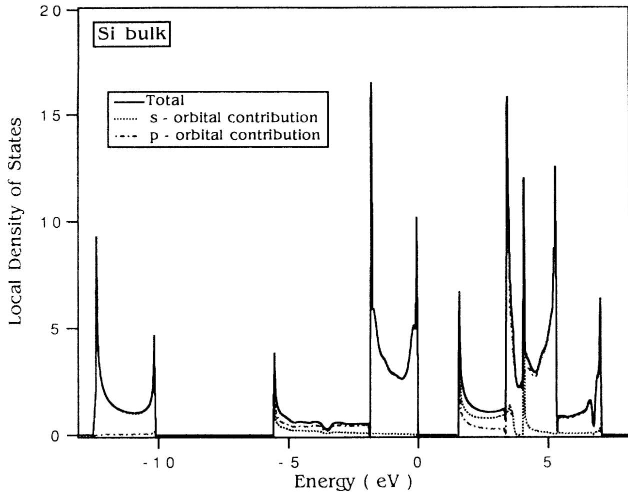

FIG. 2. Bulk Si LDOS/eV-cell at $\bar{\Gamma}$ given by the band structure of Fig. 1. The s-wave contribution is given by the dotted curve, the p-wave contribution by the dot-dashed curve, and the total by the solid curve.

form, does not include surface reconstruction, V, in principle, can incorporate two important features: (1) the breaking of the bonds across the cleavage plane (i.e., between layers $n=0$ and -1); and (2) the perturbation of the atoms in the surface layer due to the formation of the surface. The first of these features can be represented mathematically by writing

$$h(0,-1)=h(-1,0)=0\ , \tag{4}$$

i.e.,

$$V(0,-1)=-H(0,-1),\quad V(-1,0)=-H(-1,0)\ . \tag{5}$$

Geometrically, in the surface layer of Si(111), each atom is surrounded by a hexagonal arrangement of six other atoms, and this pattern is repeated in successive planes parallel to the surface [i.e., the (111) direction]. Moreover, the stacking of the planes is such that of the four nearest neighbors (nn) of a particular atom, three are located in one of the adjacent planes, and the fourth in the other one. Thus, in principle, there are two possible ways to form the surface, namely by cutting either one or three nn bonds per atom. In practice, however, only the former situation occurs, which is what we consider in this paper. The other properties represented by V in (3) are the surface perturbations, which are of two types. First, the shift in the energy levels of the surface atoms is an additive term δ (independent of $\mathbf{k}$), which affects only the atoms in the surface layer. Thus

$$V(0,0)_{\alpha 0,\alpha 0}=\delta\ , \tag{6}$$

with $\alpha=s$, x, y, and z, an orbital index. Second, the surface relaxation is modeled by scaling the nn [and second-nearest-neighbor (2nn)] terms, between the surface and first interior double layers, by a factor d (d'), which is the ratio of the new interaction to the old one; i.e., for $V(0,0)$ we obtain

$$V(0,0)_{\alpha\nu,\alpha'\nu'}=(d-1)H(0,0)_{\alpha\nu,\alpha'\nu'}\ \text{ for } \nu\neq\nu'\ . \tag{7}$$

Because of the inclusion of 2nn in this paper, additional matrix elements are present for $V(-1,0)$. Furthermore, $V(1,0)$ and $V(0,1)$ are nonzero and must also be determined.

It is now a straightforward, but tedious, procedure to calculate, in mixed basis representation, the matrix elements of V required in (5) and (7).[11] With these in hand, it is possible to calculate the surface GF, g, from the Dyson equation (2). For the scattering potential used here, (2) leads to the 8×8 matrix equation

$$g(n,n')=G(n,n')+[G(n,-1)V(-1,0)+G(n,0)V(0,0)+G(n,1)V(1,0)]g(0,n')+G(n,0)V(0,1)g(1,n')\quad (n,n'\geq 0)\ . \tag{8}$$

Once the relevant matrix elements of the bulk GF, G, and potential V are calculated, it is a simple matter of matrix algebra to calculate the GF, g, for the cleaved crystal at any desired double layer n. The corresponding LDOS for that layer and for a particular $\mathbf{k}_{\parallel}$ is then given by

$$\rho_n(E,\mathbf{k}_{\parallel})=-\frac{1}{\pi}\mathrm{Im}\,\mathrm{Tr}\,g(E,n,n',\mathbf{k}_{\parallel})\ . \tag{9}$$

III. RESULTS

Turning now to some numerical results, we first examine the density of states in the surface layer, at the SBZ center $\bar{\Gamma}$ ($\mathbf{k}_{\parallel}=\mathbf{0}$), in the case of an unreconstructed surface ($\delta=0,d=1,d'=1$) shown in Fig. 3(a). A surface state corresponding to the dangling bond created when the crystal is cleaved perpendicular to the (111) direction is found in the band gap. Figure 3(b) shows the same calculation with a 0.33-Å relaxation of the surface atoms ($\delta=0,d=1.08,d'=1.145$) as predicted by Appelbaum and Hamann (AH).[12] The surface state is found at 0.98 eV above the valence band. This is in close agreement with AH and Pandey and Phillips (PP),[13] who showed the surface state at 0.88 and 1.04 eV, respectively, above the valence band. Table III shows the location of the surface state and two other localized states below the valence-band edge found in the present paper and compared with those of AH and PP.

Calculations were performed for the arsenic-passivated

TABLE III. Comparison of the energy levels of a surface state in the band gap and two localized states below the valence-band edge, in eV, at the $\bar{\Gamma}$ point in the SBZ of relaxed (0.33 Å) Si(111).

Appelbaum and Hamann	This work	Pandey and Phillips
0.88	0.98	1.04
−1.95	−1.82	−1.71
−12.90	−12.40	−12.87

silicon (111) surface, an example of an unreconstructed surface, which permits direct comparison with experimental results. The tight-binding parameters for the As atom were determined from data given in Ref. 10 and are shown in Table I. Since the presence of the As at the outermost layer is treated as a surface perturbation in our formulation, we can still use Eq. (8) with a different set of nonzero $V(0,0)$, $V(1,0)$ and $V(0,1)$ for the GF of the combined As-Si(111) system. Various authors[10,14] have found different values for E_S and E_p for silicon and arsenic. The δ_s and δ_p parameters used for our calculations ($\delta_s=-3.78$ eV and $\delta_p=-2.46$ eV, as shown in Table I) are within the variation given in Refs. 10 and 14 and provide a good fit to the two experimental states below the valence-band edge and to the state in the band gap.

The scaling parameters d and d' used in calculating the scattering potential are obtained from the following argument. It has been noted[4] that the expansion of the As layer at the surface is 0.24 Å. This implies that the As-Si nearest-neighbor distance is $h'=2.44$ Å, compared to the Si-Si distance $h=2.35$ Å. According to Harrison,[10] all the bond strengths should go as $1/h^2$, so the ratio of Si-As to Si-Si should be $d=(2.35/2.44)^2=0.928$. Similarly, d' is determined to be 0.904. All matrix elements of the scattering potential for the As surface layer may thus be calculated.

The LDOS calculated for the As-passivated Si surface layer at the $\bar{\Gamma}$ point is shown in Fig. 4. For comparison of the results, it is appropriate to relate the surface and localized states to the nearest band edges. A surface state ($S1$) occurs in the band gap at 0.76 eV below the conduction band. This checks with Becker *et al.*,[3] who show a state at about 0.6 eV below the conduction band. Two other localized states appear in the valence band. As shown in Fig. 4, the first state ($S2$) is located very close to the valence-band edge and the second state ($S3$) is located ~0.3 eV below the bottom of the first valence band. These correspond to the two states in the valence band observed by Uhrberg *et al.*[2] at ~0.3 eV below the valence-band edge and ~0.1 eV below the bottom of the first valence band. In our calculation we find another localized state ($S4$) at 3.06 eV above the bottom of the conduction band. It appears that the previous investigators have not studied the conduction band of this system in

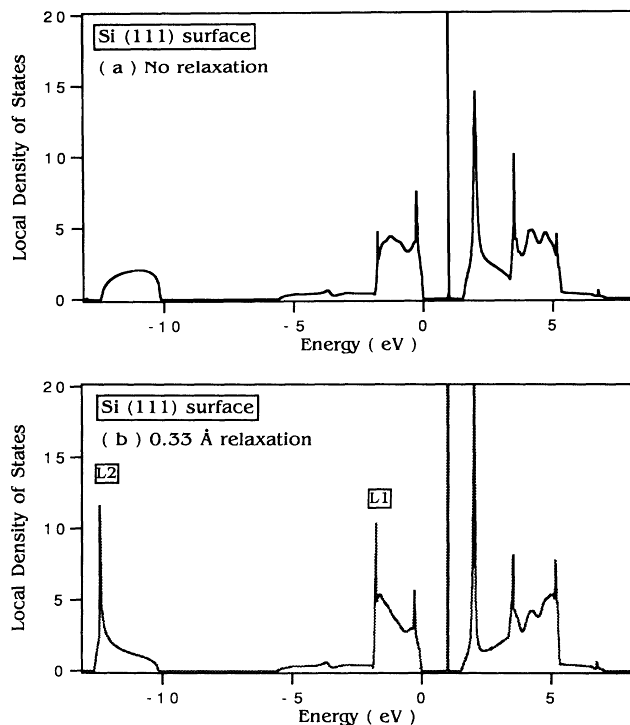

FIG. 3. (a) LDOS/eV-cell of Si(111) surface layer at $\bar{\Gamma}$ for the unperturbed and unrelaxed ideal 1×1 surfaces ($\delta=0, d=1, d'=1$). (b) LDOS/eV-cell of Si(111) surface layer at $\bar{\Gamma}$ for the 0.33-Å relaxed surface ($\delta=0, d=1.08, d'=1.145$). Note that a gap state appears at 0.98 eV above the valence-band edge in both cases, and two localized states appear below the valence-band edge in the latter case, in agreement with Appelbaum and Hamann and Pandey and Phillips.

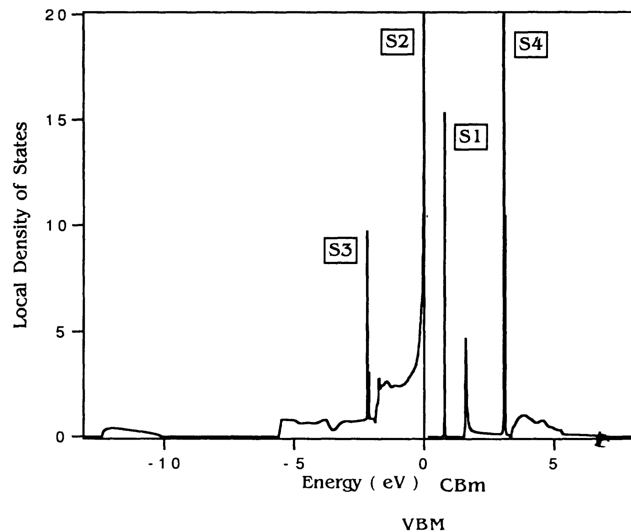

FIG. 4. LDOS/eV-cell of As-Si surface at $\bar{\Gamma}$. There is one state ($S1$) in the band gap and two resonance states ($S2$ and $S3$) below the valence-band maximum (VBM). Another state ($S4$) is shown above the conduction-band minimum (CBM). Also note the modification of the bulk states from the pure silicon cases shown in Fig. 3.

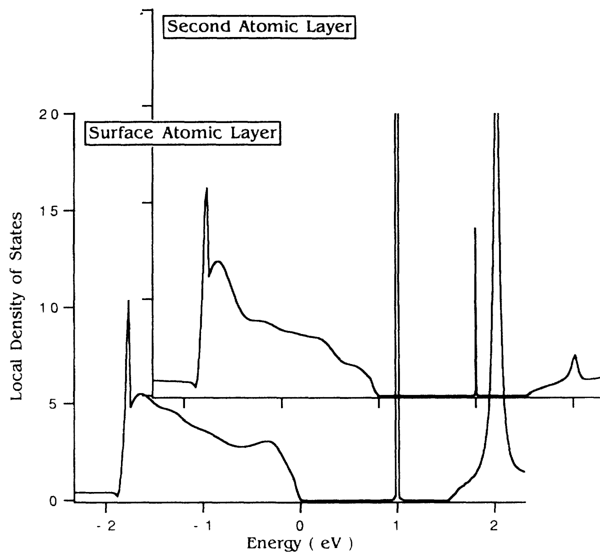

FIG. 5. LDOS/eV-cell of Si(111) surface layer and subsurface layer at $\bar{\Gamma}$ for the 0.33-Å relaxed surface near the band gap, showing how the localized states decay into the bulk.

detail and thus do not report this state. All of the states mentioned exhibit a p-like character except the state in the gap ($S1$) which is predominantly s like at the surface.

Since our method allows us to calculate how the localized states decay into the bulk, we have calculated the strength and position of the gap state of the relaxed silicon surface in the first interior layer, which is shown along with the nearby bulk states in Fig. 5. As anticipated, the strength of the surface state is indeed significantly lowered in the first interior layer. A similar calculation of the gap state in the first and second interior layers for the As-Si sample has been carried out. We find that the strength of the gap state in the first three layers varies approximately as 1.0:2.0:0.5, which implies that the gap state in the As-passivated sample first grows in strength in the first silicon interior layer before decreasing in the second and subsequent inner layers. The reason for the enhancement of the gap state in the first silicon interior layer can be understood on the basis of the larger contribution of the p states in the subsurface silicon layer as discussed by Becker *et al.*[3] This is consistent with our findings that this state, which is predominantly s like at the surface, becomes more p like in character in the interior layers.

IV. DISCUSSION

In this paper we have extended the silicon empirical tight-binding Hamiltonian of CC by incorporating two extra 2nn terms. The band structure obtained by using this Hamiltonian has a much better agreement in the conduction band with the EPM calculation of Chelikowsky and Cohen[9] than that of CC. Then, using the Green's-function method to this Hamiltonian, we have calculated the LDOS of the bulk sample at the $\bar{\Gamma}$ point [(111) direction] which showed the usual van Hove singularities. Our method also allowed us to distinguish between the s and p contributions to the LDOS as shown in Fig. 2. We next proceeded to calculate the LDOS at the pure unreconstructed Si(111) surface layer of a semi-infinite slab. We notice that the dangling bond at the surface creates a state inside the band gap, the location of which agrees well with that calculated by AH and PP. Like AH and PP, we also observe two other localized states at lower energies when the top layer of atoms is allowed to have an inward relaxation of 0.33 Å. We then studied the more interesting case of the As-passivated Si(111) surface of a semi-infinite sample which is experimentally known to remain unreconstructed. Our calculation shows that arsenic produces an unoccupied surface state in the band gap and two resonance states inside the valence band. The locations of these states have a close correspondence with those found in previous experimental studies.[1-4] The two resonance states inside the valence band were also verified by a pseudopotential calculation.[2] The state inside the gap and the resonance state near the top of the valence band were calculated by a self-energy method using a repeated slab geometry to represent the surface.[3] Our method reproduces all three states, since to our knowledge it is the only calculation which covers the valence band, the band gap, and the lower conduction band. Furthermore, our calculation predicts another localized state in the conduction band which has so far remained unnoticed, since this region of the conduction band has not been carefully studied either theoretically or experimentally. Finally we would like to point out that our ETB-GF method allows the study of a truly semi-infinite sample (unlike most other theoretical studies which usually deal only with finite slabs) and a calculation of not only the positions of the localized states but also their strengths and how they decay into the bulk. This ETB-GF method can also be used to calculate densities of the bulk states at each layer along with the individual contributions of the various atomic orbitals, and how these bulk states are modified by the presence of the surface. To our knowledge, no other theoretical approach simultaneously addresses all three of these features.

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