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Electron states at planar and stepped semiconductor surfaces

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We develop a method to study electronic properties of planar and stepped semiconductor surfaces. The method, based on the Bethe-Peierls approximation, deals with tight-binding Hamiltonians, and since it works in a real-space representation, avoids numerical integrations in k space to get the density of states. We calculate the electronic density of states at steps in the (11) surface in the honeycomb lattice as well as in the (111) surface of a covalent semiconductor (Si, Ge). Our results in the latter case are in good agreement with ultraviolet photoemission data.

I. INTRODUCTION

There are many situations in solid-state physics in which the simplification provided by the use of Bloch states cannot be incorporated in a simple way in the calculations due to the lack of periodicity in the problem. Among these situations we can mention impurities, surfaces, vacancies, amorphous systems, etc.

In this work we shall concentrate on the calculation of the electronic density of states in a situation in which these complications are patent, namely, the study of stepped semiconductor surfaces. In addition to the problems inherent to the study of surfaces, the two-dimensional periodicity of the surface is broken by the presence of the steps.

One way to handle these situations, taking advantage of the simplifications of the use of Bloch states, has been to artificially repeat the local deviation from periodicity to build up a periodic structure, and then perform a band-structure calculation.[1] The main drawback of such an approach is that the artificial periodicity can introduce spurious structure in the density of states. In addition, the unit cell has to be very large and the computation is very involved and lengthy. In spite of these shortcomings this approach has been very successful in the study of amorphous semiconductors,[2] surfaces,[3] etc.

Another approach developed with the same purpose has been proposed. This is the so-called recursion method[4] that takes advantage of the rapid convergency of continued fractions and spans the Green's function in a continued fraction such that its coefficients are constant beyond a certain level. This approximation has been very useful in the study of "local" deviations from periodicity[5] (like amorphous semiconductors). Using this, approximation steps in transition-metal surfaces have been studied.[6]

Finally, another way to study nonperiodic structures consists of picking up a cluster of atoms which includes the local problem to be treated and attaching at the cluster's surfaces the Bethe lattice.[2,7] One then ends up with a cluster–Bethe-lattice model. This approach, as it stands, does not seem to be useful in the study of "extended" perturbations like surfaces.

To overcome the inability of the cluster–Bethe-lattice model to study delocalized perturbations, we extend it in this work to study surfaces,[8] with the final aim of calculating densities of states at steps in Si and Ge (111) surfaces. The way to solve for the *surface* Bethe lattice is to reduce the three-dimensional problem to a two-dimensional system in such a way that one of its sides is connected to the *bulk* Bethe lattice, whereas the other side is kept free. The resulting system can be solved by means of the transfer-matrix technique to get the local Green's function and from it the density of states is obtained immediately.

The format of this paper is as follows: To gain some insight into the problem of steps in Si and Ge, we study in Sec. II the density of states in a step in the (11) surface of the honeycomb lattice. To make the calculation simple, we focus our attention on a simple sp^2 Hamiltonian. In Sec. III we work out in detail the case of a step in the (111) surface of Si. In this case we work with a realistic sp^3 Hamiltonian. Comparison with ultraviolet-photoemission-spectroscopy experimental data is also made. Finally, in Sec. IV, a summary of the more relevant results that we have obtained is made. Some conclusion remarks are presented as well.

II. METHOD OF CALCULATION: HONEYCOMB LATTICE

In order to discuss the method of calculation and at the same time to gain some insight into the

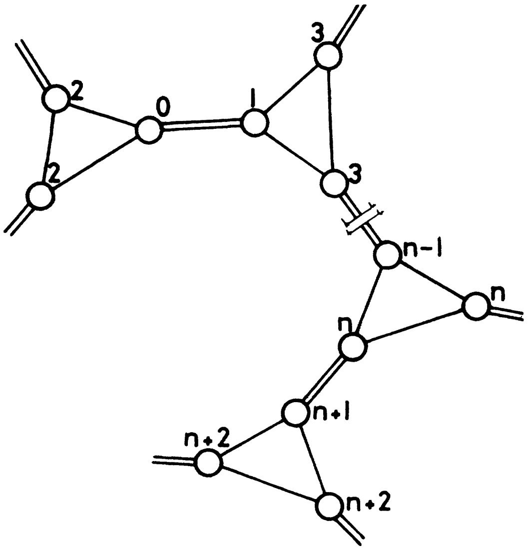

FIG. 1. Honeycomb Bethe lattice interaction diagram for the Hamiltonian of Eq. (1). The circles represent sp^2 orbitals, the double lines represent the interaction V_1, and the single lines represent the interaction V_2.

problems of steps, we first study the (11) surface of the honeycomb lattice. We focus our attention on an sp^2 Hamiltonian[9] analogous to the sp^3 Weaire-Thorpe Hamiltonian.[10] This sp^2 Hamiltonian has the following form:

$$H = V_1 \sum_{j, i \neq i'} |ij\rangle\langle i'j| + V_2 \sum_{i, j \neq j'} |ij\rangle\langle ij'| , \quad (1)$$

where ij represents the sp^2 orbital at atom i and bond j. The sums in (1) are restricted to nearest-neighbor atoms only. V_1 represents the intrabond interaction, whereas V_2 represents the intra-atomic interaction.

To solve for the bulk Bethe lattice we follow the usual prescription.[7] Looking at Fig. 1, we can write the following set of equations:

$$\begin{aligned}
&E g_{0,0} = 1 + V_1 g_{1,0} + 2V_2 g_{2,0} , \\
&E g_{1,0} = V_1 g_{0,0} + 2V_2 g_{3,0} , \\
&E g_{2,0} = V_2 g_{0,0} + V_2 g_{2,0} + V_1 g_{4,0} , \\
&\vdots \qquad \vdots \qquad \vdots \qquad \vdots \\
&E g_{n,0} = V_2 g_{n-1,0} + V_2 g_{n,0} + V_1 g_{n+1,0} , \\
&E g_{n+1,0} = V_1 g_{n,0} + 2V_2 g_{n+2,0} ,
\end{aligned} \quad (2)$$

where $g_{i,0}$ represents the matrix element of the Green's function between the orbital labeled 0 and the orbital labeled i. We then define the transfer functions α and β by

$$\alpha = g_{n,0}/g_{n-1,0}, \quad \beta = g_{n+1,0}/g_{n,0} , \quad (3)$$

which are the solutions of

$$(E - V_2)\alpha = V_2 + V_1\alpha\beta, \qquad E\beta = V_1 + 2V_2\alpha\beta . \quad (4)$$

Once we know how to solve the bulk, we proceed to study the surface. A portion of the surface Bethe lattice is drawn in Fig. 2. The generic equations of the surface Bethe lattice are of the following form:

$$\begin{aligned}
&\vdots \qquad\qquad \vdots \qquad\qquad \vdots \\
&\left(E - \frac{V_2^2}{E - V_1\beta}\right) g_{n-1,0} = V_1 g_{n-2,0} + \left(V_2 + \frac{V_2^2}{E - V_1\beta}\right) g_{n,0} , \\
&\left(E - \frac{V_2^2}{E - V_1\beta}\right) g_{n,0} = \left(V_2 + \frac{V_2^2}{E - V_1\beta}\right) g_{n-1,0} + V_1 g_{n+1,0} , \\
&\left(E - \frac{V_2^2}{E}\right) g_{n+1,0} = V_1 g_{n,0} + \left(V_2 + \frac{V_2^2}{E}\right) g_{n+2,0} , \\
&\left(E - \frac{V_2^2}{E}\right) g_{n+2,0} = \left(V_2 + \frac{V_2^2}{E}\right) g_{n+1,0} + V_1 g_{n+3,0} . \\
&\vdots \qquad\qquad \vdots \qquad\qquad \vdots
\end{aligned} \quad (5)$$

We can solve (5) by defining the following transfer functions

$$\begin{aligned}
&T^{\text{out}} \equiv g_{n+1,0}/g_{n,0}, \quad T^{\text{in}} \equiv g_{n+3,0}/g_{n+2,0} , \\
&T_1 \equiv g_{n+2,0}/g_{n+1,0}, \quad T_2 \equiv g_{n,0}/g_{n-1,0} .
\end{aligned} \quad (6)$$

Substitution of these functions back into (5) yields a simple equation for each transfer function.

Once the transfer functions are known, the density of states at a particular orbital is obtained immediately by means of the diagonal matrix of the Green's function.

The local Green's function of, say, the dangling orbital is then given by

$$\langle dg|G|dg\rangle = 1/[E - 2V_2^2/(E - V_2 - V_1 T^{\text{in}})] . \quad (7)$$

Results for the density of states of an orbital at the bulk and at various orbitals in the vicinity of the surface are drawn in Fig. 3. In this case we take for the parameters in the sp^2 Hamiltonian $V_1 = -6$ eV and $V_2 = -2$ eV. We first notice the presence of a δ-function contribution to the bulk density of states; this corresponds to a noninter-

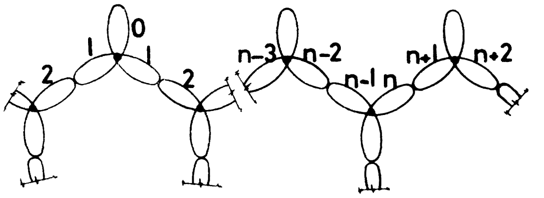

FIG. 2. Labeling of the sp^2 orbitals used to solve the honeycomb surface Bethe lattice.

acting p-bonding state. This zero-width band is due to the neglect of the $pp\pi$ interaction in the Hamiltonian (1). The gap in the density of states is between -4 and ~ 2.5 eV.

The densities of states for orbitals in the vicinity of the surface display several interesting features: (i) The density of states of the dangling bond presents a band in the middle of the band gap. The states associated with this band decay very rapidly into the bulk [see the sequence Fig. 3(a), (b), and (c)]. (ii) The states associated with this band are sp^2 in character. (iii) The shape of the dangling-bond density of states is very similar to the *exact* density of states.[9] (iv) There is a surface contribution to the density of states in the middle of the valence band at ~ -7.0 eV. The states associated with this feature are mostly atomic s-like states and correspond to the state discussed in detail in Ref. 11. It is striking that even though the Bethe lattice does not present gaps in the valence band, true bona fide surface states can exist. This can be even more clear working with a simple s-state Hamiltonian. The state corresponding to the peak at -7 eV in Fig. 3 appears as a peak with in-

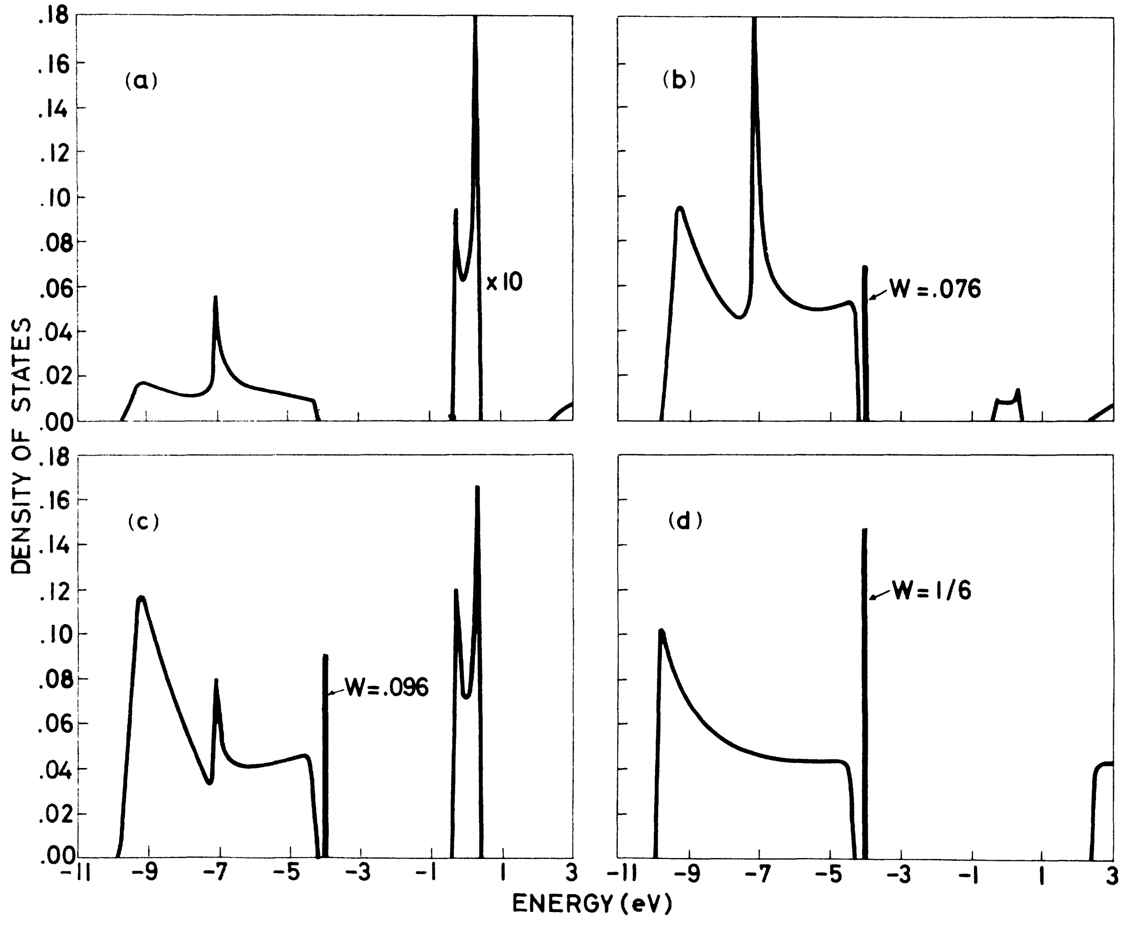

FIG. 3. Local densities of states at various sp^2 orbitals in the vicinity of the (11) surface of the honeycomb lattice within the Bethe-lattice approximation. (a) Local density of states at the dangling bond (labeled 0 in Fig. 2). (b) Local density of states at orbital labeled 1 in Fig. 2. (c) Local density of states at orbital labeled 2 in Fig. 2. (d) Local density of states at an orbital in the bulk. The heavy vertical straight lines indicate the p-bonding band, and W represents the corresponding weight. All the curves are normalized to one.

finite height (i.e., no interaction with the bulk). (v) The behavior of the p-like δ function at -4 eV is very similar to the *exact* behavior.[9]

The agreement between our approximated calculation and the exact results gives us confidence in the Bethe-lattice approximation. We can then proceed to study the density of states associated with a step in an otherwise planar surface.

The procedure to calculate the density of states follows the cluster-Bethe-lattice method spirit.[2] The step plays the role of the cluster and at its edges we attach the corresponding Bethe lattice (i.e., surface or bulk Bethe lattice). The cluster we have taken is drawn in Fig. 4. We attach the bulk Bethe lattice at orbitals labeled 8 and 10. On the other hand, we attach the surface Bethe lattice to the orbitals labeled 1 and 14. The problem then has been reduced to finding the solution of a finite system of linear equations.

Results of our calculations are drawn in Fig. 5. We present local densities of states in Fig. 4 at orbitals labeled 0, 4, and 13, respectively. Looking at this figure we notice two important facts. First, the dangling-bond band splits into two δ functions [see Fig. 5(a) and (b)], one above the original dangling-bond band and the other one below it. The states associated with these δ functions are localized in dangling bonds labeled 0 and 4 in Fig. 4. The origin of this behavior is the stronger interaction between dangling bonds 0 and 4 than the nearest-neighbor dangling-bond interaction in the planar surface. This interaction gives rise to a bonding-antibonding splitting. Second, another interesting result of our calculation is the change in the shape of the dangling-bond band in the orbital labeled 13 in Fig. 4. This local density of states shows an increase at the middle of the band [see Fig. 5(c)] and a disappearance of the band-edge singularity. This behavior is due to the end of the one-dimensional chain of dangling bonds due to the presence of the steps.

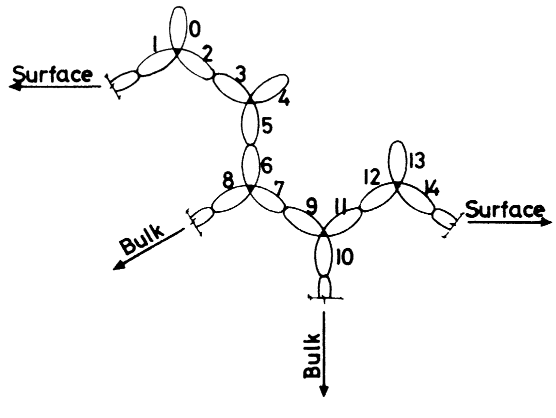

FIG. 4. Labeling of the sp^2 orbitals in the step in the (11) surface of the honeycomb lattice.

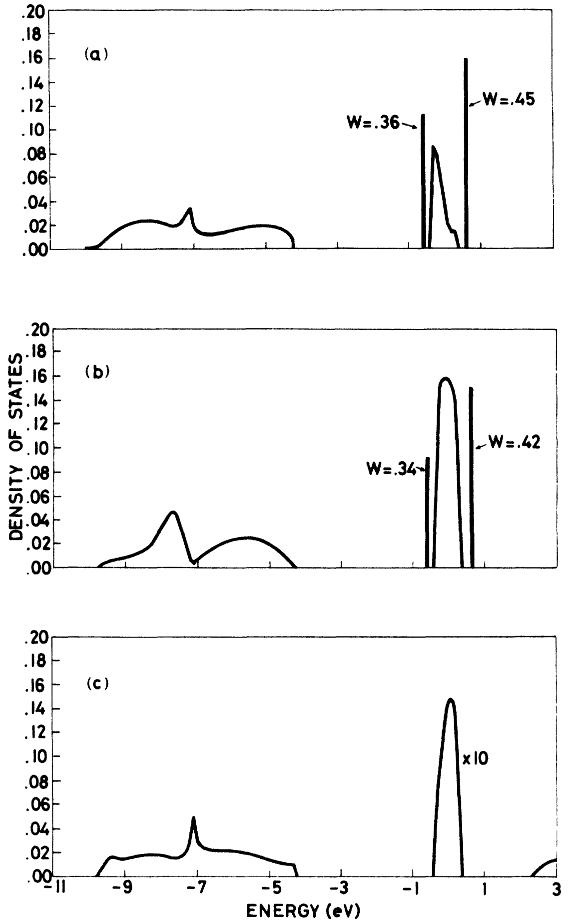

FIG. 5. Local densities of states at various sp^2 orbitals in the step drawn in Fig. 4. (a) Local densities of states at orbital labeled 0 in Fig. 4. (b) Local density of states at orbital labeled 4 in Fig. 4. (c) Local density of states at orbital labeled 13 in Fig. 4. The heavy vertical straight lines indicate δ-function contributions to the density of states. Their corresponding weight is also indicated in the drawings. All the curves are normalized to one.

We see that the presence of the step in the surface gives rise to very pronounced changes in the density of states at atoms in the step. Whether or not these results have some relation to the actual density of states at steps in semiconductors will be apparent when discussing more realistic models. We would just like to advance that the aforementioned results are very similar in essence to those obtained in a realistic calculation.

III. DIAMOND LATTICE: REALISTIC HAMILTONIAN

To study the electronic structure of planar and stepped semiconductor surfaces we shall use in this section a realistic tight-binding Hamiltonian which takes into account all possible interactions between *s* and *p* atomic orbitals in nearest-neighbor atoms. The Hamiltonian includes then the *ssσ*, *spσ*, *ppσ*, and *ppπ* interactions in the Koster-Slater notation.[12] Since the Hamiltonian has been described elsewhere,[13-16] we will not go into details. The parameters we have taken in our calculations are given in Table I. They are appropriate to both Si and Ge. Since we are not aiming for a very accurate calculation, our parameters serve as a prototype for group-IV covalence semiconductors.

In our calculations we work with the directed sp^3 hybridized orbitals. As we did in Sec. II, we first solve the bulk and then the surface. The solution of the bulk has been published elsewhere,[16] so we just give an outline of it. We call 1, 2, 3, and 4 the four bond directions in the diamond structure, and $\underline{T}_1$, $\underline{T}_2$, $\underline{T}_3$, and $\underline{T}_4$ the corresponding transfer matrices in the Bethe lattice. The local Green's function at an atom (labeled 0) in the bulk is given by the solution of

$$(\underline{1}E-\underline{U}_0)G^B_{0,0}=\underline{1}+\sum_{i=1}^{4}\underline{U}_i\cdot\underline{M}_i^{-1}\cdot\underline{T}_1\cdot\underline{M}_i\cdot\underline{G}_{0,0}\,, \tag{8}$$

where the matrix $\underline{U}_i(i=1,2,3,4)$ is formed by the matrix elements of the Hamiltonian between the sp^3 orbitals in one atom and those in its nearer-neighbor atom along the direction of the bond $0j$. The matrix $\underline{U}_0$ contains the intra-atomic interaction between sp^3 orbitals in an atom. The matrices $\underline{M}_i$ correspond to the symmetry operation of the diamond structure. The transfer matrix $\underline{T}_1$ is given by

$$(\underline{1}E-\underline{U}_0)\cdot\underline{T}_1=\underline{U}_1+\sum_{i=2}^{4}\underline{U}_i\cdot\underline{M}_i^{-1}\cdot\underline{T}_1\cdot\underline{M}_i\cdot\underline{T}_i\,. \tag{9}$$

TABLE I. Values (in eV) of the tight-binding Hamiltonian used to study the covalent semiconductor surface.

E_p-E_s	*ssσ*	*spσ*	*ppσ*	*ppπ*
8.000	−1.650	−2.165	−3.350	−1.000

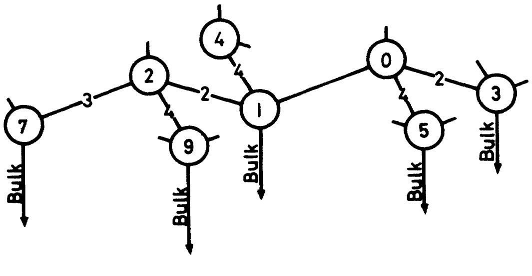

FIG. 6. Portion of the (111) surface Bethe lattice for the diamond structure. The circles indicate the atoms. Numbers in the bonds indicate bond direction.

Once we know the bulk transfer matrix, the solution of the surface follows the steps described in Sec. II for the honeycomb lattice. We assume that the (111) surface is normal to the bonds labeled 1. If we label the atoms at the surface in the way shown in Fig. 6, we get the following infinite set of equations for the matrix elements of the Green's function:

$$\begin{aligned}
(\underline{1}E-\underline{U}_0^s)\cdot\underline{G}^s_{0,0}&=\underline{1}+\underline{U}_3\cdot\underline{G}^3_{1,0}+\underline{U}_2\cdot\underline{G}^2_{3,0}+\underline{U}_4\cdot G^4_{5,0}\,,\\
(\underline{1}E-\underline{U}_0-\underline{U}_1\cdot\underline{T}_1)\cdot\underline{G}^3_{1,0}&=\underline{U}_3\circ\underline{G}_{0,0}+\underline{U}_2\cdot\underline{G}^2_{2,0}+\underline{U}_4\cdot\underline{G}^4_{4,0}\,,\\
(\underline{1}E-\underline{U}_0^s)\cdot\underline{G}^2_{2,0}&=\underline{U}_2\cdot\underline{G}^3_{1,0}+\underline{U}_3\cdot\underline{G}^3_{7,0}+\underline{U}_4\cdot\underline{G}^4_{9,0}\,,\\
&\vdots\qquad\vdots\qquad\vdots\qquad\vdots
\end{aligned} \tag{10}$$

where $\underline{U}_0^s$ indicates that the intra-atomic interactions at the surface might be different from the corresponding interactions in the bulk.

To solve the system of linear equations (10) we define, as we did in the case of the honeycomb lattice, the following transfer matrices:

$$\underline{\tau}^{\text{in}}_{2,3,4}\equiv\underline{G}^{2,3,4}_{j',0}\cdot(\underline{G}^{2,3,4}_{j,0})^{-1}\,, \tag{11a}$$

$$\underline{\tau}^{\text{out}}_{2,3,4}\equiv\underline{G}^{2,3,4}_{j,0}\cdot(\underline{G}^{2,3,4}_{j',0})^{-1}\,, \tag{11b}$$

where j and j' are nearest-neighbor atoms, j being even and j', odd. Insertion of (11a) and (11b) in (10) gives us the following equations for $\underline{\tau}^{\text{in}}$ and $\underline{\tau}^{\text{out}}$:

$$\begin{aligned}
\underline{\tau}_2^{\text{in}}&=(\underline{1}E-\underline{U}_0-\underline{U}_1\cdot\underline{T}_1-\underline{U}_3\cdot\underline{\tau}_3^{\text{out}}\\
&\qquad-\underline{U}_4\cdot\underline{S}_1^{-1}\cdot\underline{\tau}_3^{\text{out}}\cdot\underline{S}_1)^{-1}\cdot\underline{U}_2\,,\\
\underline{\tau}_3^{\text{out}}&=(\underline{1}E-\underline{U}_0^s-\underline{U}_2\cdot\underline{\tau}_2^{\text{in}}-\underline{U}_4\cdot\underline{S}_2^{-1}\cdot\underline{\tau}_2^{\text{in}}\cdot\underline{S}_2)^{-1}\cdot\underline{U}_3\,.
\end{aligned} \tag{12}$$

The other transfer matrices $\tau_{3,4}^{\text{in,out}}$ are obtained from $\tau_2^{\text{in,out}}$ by applying the symmetry operations of the (111) surface of the diamond structure:

$$\begin{aligned}
\underline{\tau}_3^{\text{in,out}}&=\underline{S}_3^{-1}\cdot\underline{\tau}_2^{\text{in,out}}\cdot\underline{S}_3\,,\\
\underline{\tau}_4^{\text{in,out}}&=\underline{S}_2^{-1}\cdot\underline{\tau}_2^{\text{in,out}}\cdot\underline{S}_2\,.
\end{aligned} \tag{13}$$

The local Green's function of an atom at the surface is then given by

$$\underline{G}^s_{0,0}=(\underline{1}E-\underline{U}_0^s-\underline{U}_2\cdot\underline{\tau}_2^{\text{in}}-\underline{U}_3\cdot\underline{\tau}_3^{\text{in}}-\underline{U}_4\cdot\underline{\tau}_4^{\text{in}})^{-1}\,. \tag{14}$$

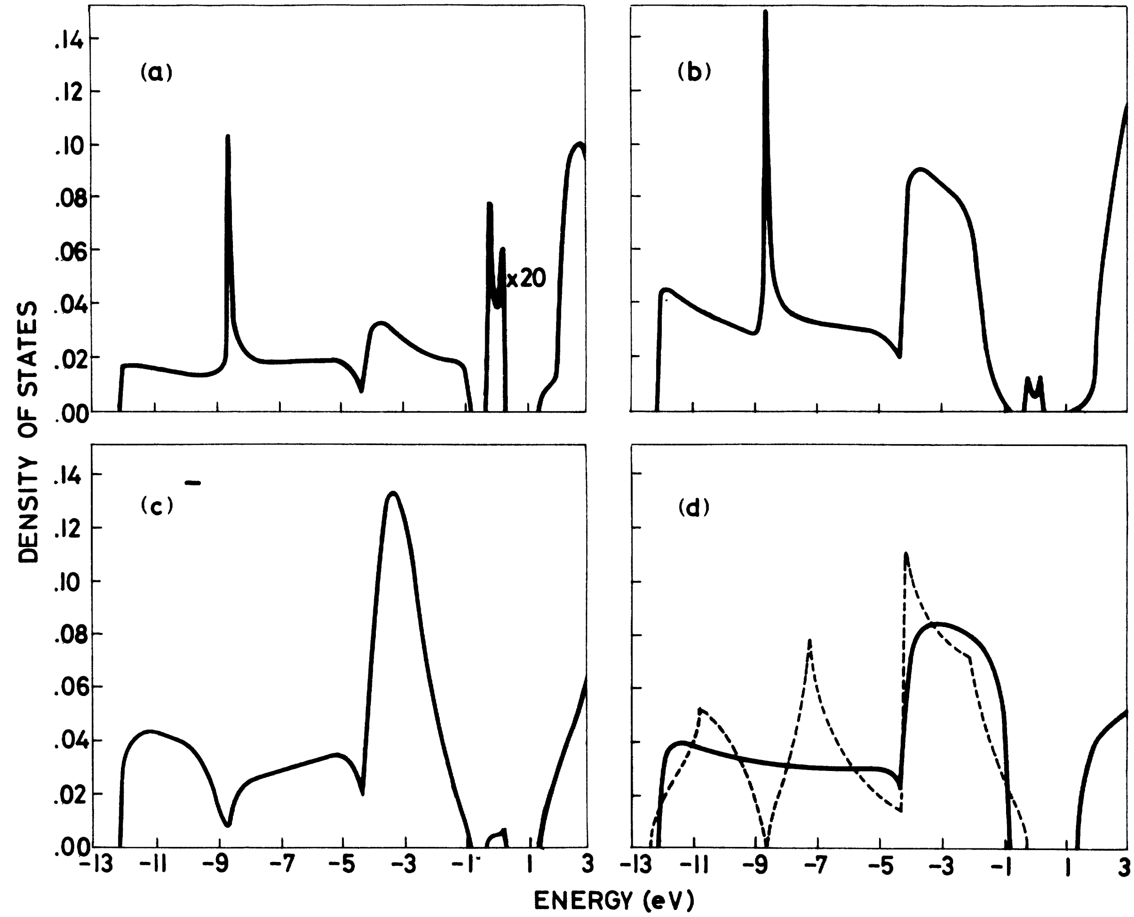

FIG. 7. Local densities of states at various sp^3 orbitals in the vicinity of the (111) surface of the diamond lattice within Bethe-lattice approximation. (a) Local density of states at the dangling bond. (b) Local density of states at the back sp^3 orbitals of the surface atoms. (c) Local density of states at the sp^3 orbitals forming a bond with the previous ones. (d) Local density of states at an orbital in the bulk (solid line). Crystal density of states (broken line) for the same Hamiltonian. All the curves are normalized to one.

We obtain similar equations for atoms in different layers. Once the local Green's function is known, the local density of states is given by the standard equation

$$n_0(E) = -\Pi^{-1}\mathrm{Im}\{\mathrm{Tr}[G_{0,0}(E)]\} . \qquad (15)$$

In our calculation of the density of states at the surface we shift downward the sp^3 orbital energy at the surface atoms by 0.5 eV in order to get charge neutrality.[17]

Results of our calculation are shown in Fig. 7, where we have drawn the local densities of states at various layers near the surface and at the bulk. In this figure we note (i) There is a dangling-bond band in the middle of the gap [See Fig. 7(a)]; the states associated with this band are mostly (almost 100%) localized in the dangling sp^3 orbital pointing out from the surface. (ii) There is a band of surface states in the middle of the valence band [see Fig. 7(a) and (b)] at energies where the crystal density of states presents a dip [see Fig. 7(d)]. These states are s states localized in the first layer with almost zero weight in the second layer. This behavior is very similar to the behavior found in an exact calculation.[11] (iii) There is an enhancement of the p-like peak in the atoms in the layer underneath the surface layer [Figure 7(c)]; the states corresponding to this feature are the so-called back bonds. All the features we have been discussing are in agreement with more detailed calculations[18] as well as with experimental data obtained by means of ultraviolet photoemission.[19] The only discrepancy with experimental results is the nonappearance in our calculation of a peak at the bottom of the valence band. The states associated with this peak might be originated by an

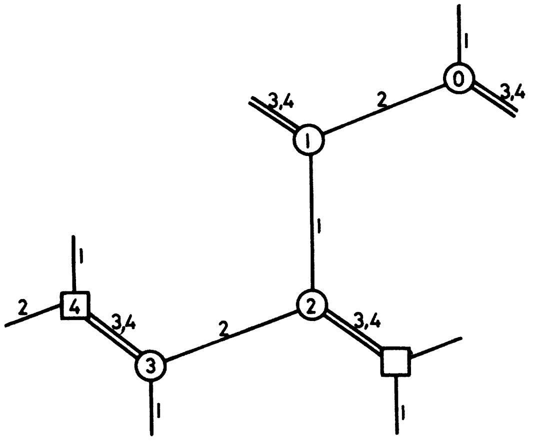

FIG. 8. Sketch of the step in the (111) surface in the diamond structure viewed along the step's edge. Numbers in the bonds indicate the bond direction.

inward relaxation of the outermost layer or by a reconstruction parallel to the surface. In the calculations corresponding to Fig. 7 we have not included these possibilities. However, if we relax inwards the surface layer we obtain the aforementioned state below the bottom of the valence band without a substantial change of the other surface states.

We can proceed now to study the density of states in a step in an otherwise perfect planar surface. The procedure is very similar to that described in Sec. II when discussing the honeycomb lattice. Here, in the case of the diamond lattice, we can distinguish two kinds of steps.[20] One kind of step presents one dangling bond per edge atom, whereas the other kind of step has two dangling bonds per edge atom. Experimentally it has been observed[20] that only steps of the second kind are present. Then we will focus our attention in steps with two dangling bonds per edge atom (see Fig. 8). In our calculations we shift the atomic potential[17] at atoms in the step by the amounts given in Table II. This is done to obtain charge neutrality. Results of our calculation are drawn in Figs. 9–12. Looking at these figures we can conclude:

(i) The dangling-bond band at the gap splits into two bands located at ~ −1.3 and 0.6 eV, respectively, [see Figs. 9(a) and (b); 10(a), (b), and (c)]. This splitting, as in the case of the honeycomb lattice, is due to the presence of two dangling bonds whose interaction is stronger than the interaction of nearest-neighbor dangling bonds in the perfect planar surface.

TABLE II. Shift of the atomic energies (in eV) introduced in the step atoms to obtain charge neutrality.

Δ0	Δ1	Δ2	Δ3	Δ4
−0.5	−1.4	0.0	0.0	−0.5

(ii) There is an enhancement of the bulk *p*-like peak at ~ −2.8 eV [Fig. 11(a)].

(iii) There is a filling up to the dangling-bond band at ~ 0 eV—compare Fig. 12(a) with Fig. 7(a). The reason for this behavior, as in the case of the honeycomb lattice, is that the dangling bond at the atom labeled 4 in Fig. 8 has two nearest-neighbor dangling bonds *less* than a dangling bond in a planar surface.

(iv) Analysis of the integrated density of states reveals that the Fermi level at a stepped surface is approximately 0.12 eV below the Fermi level at a planar surface.

All these results are in good agreement with the experimental findings.[19] In order to make a more detailed comparison with the experiments we will

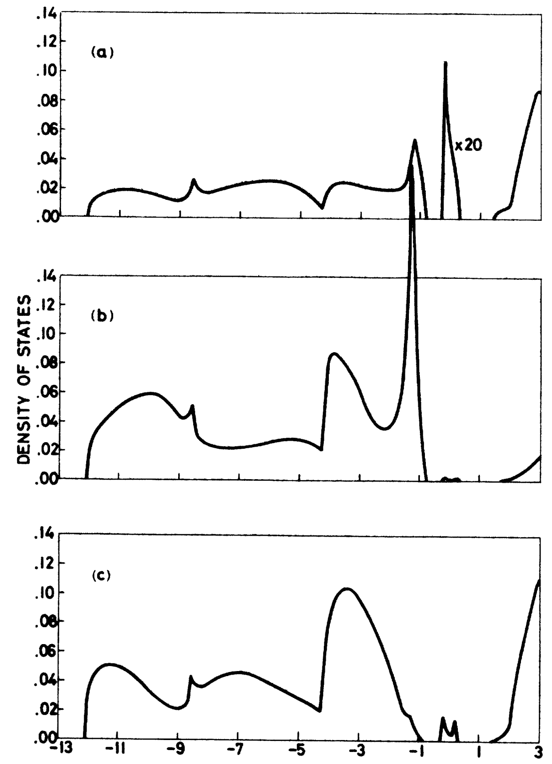

FIG. 9. Local densities of states at sp^3 orbitals in the atom labeled 0 in Fig. 8. (a) Local density of states corresponding to the orbital along the direction labeled 1 (see Fig. 8). (b) Local density of states corresponding to the orbital in the direction labeled 2. (c) Local density of states corresponding to the orbitals in the direction labeled 3 and 4. All the curves are normalized to one.

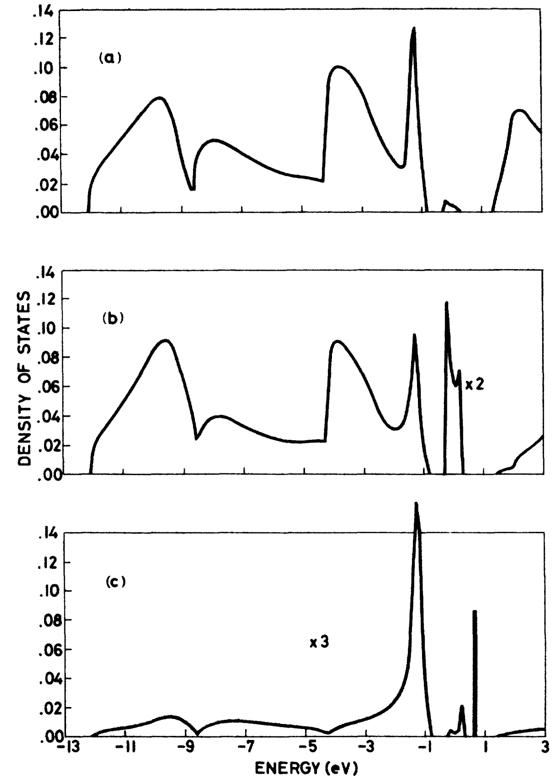

FIG. 10. Local densities of states at orbitals in atom labeled 1 in Fig. 8. (a) Local density of states corresponding to the orbital along the direction labeled 1 (see Fig. 8). (b) Local density of states corresponding to the orbital along the direction labeled 2. (c) Local density of states corresponding to the directions labeled 3 and 4. The solid vertical straight line represents a δ-function contribution to the density of states.

look in detail at the density of states close to the Fermi level. Since the states at those energies do not interact with the bulk states, the experimental resolution[19] is much higher. In order to compare with experiments we have calculated the total density at the surface and at a step in the surface. To do this we sum the contribution to the density of states corresponding to surface atoms and atoms immediately below them. We then obtain the difference between these densities of states after aligning[21] the Fermi level to its position at the step. Results of this calculation along with the experimental curve[9] are drawn in Fig. 13. We notice an excellent agreement between theory and experiments as far as the position of the peaks is concerned. This agreement might be to some extent fortuitous. Nevertheless we find that if we change the surface parameters, the position of the peaks is scarcely affected. Moreover, the physical origin of these peaks makes their existence stable against changes in the surface parameters.

Before we conclude this section, we would like to compare our results with other calculations. To our knowledge the only two published calculations of the density of states in stepped semiconductor surfaces use the technique mentioned in the introduction based in an artificial periodic structure. The introduction of this periodicity entails the presence of both "physical" and "nonphysical" steps. Rajan and Falicov[17] deal with a surface unit cell of six atoms. The Hamiltonian in the calculation is the sp^3 Weaire-Thorpe Hamiltonian.[10] Comparison to their results can only be qualitative. Even though the difference in the Hamiltonian used and the different ways to calculate the density of states, there is qualitative agreement between our calculation and Rajan and Falicov's one. Schlüter *et al.*,[22] on the other hand, perform a self-consistent calculation on a stepped surface such that the unit cell has four atoms.

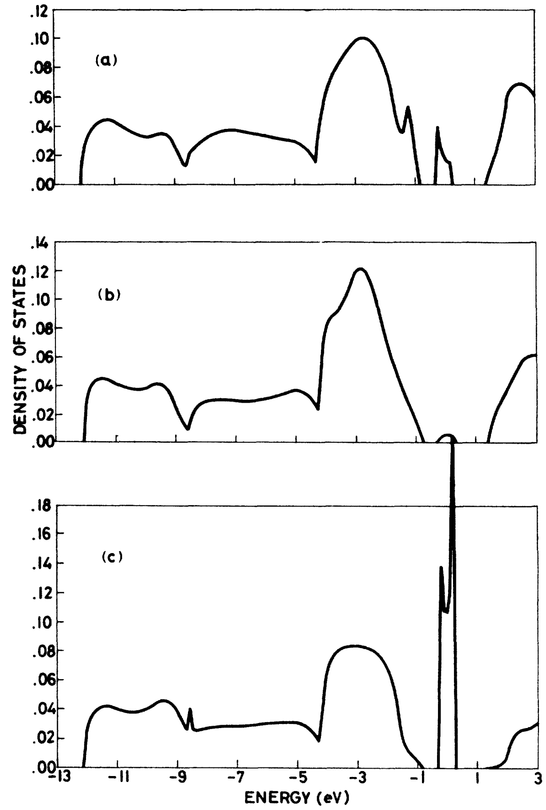

FIG. 11. Local densities of states at orbitals in atom labeled 3 in Fig. 8. (a) Local density of states corresponding to the orbital along the direction labeled 2. (b) Local density of states corresponding to the orbital along the direction labeled 1. (c) Local density of states corresponding to the directions labeled 3 and 4. The solid vertical straight line represents a δ-function contribution to the density of states.

The results of this calculation are also in agreement with our results. A detailed comparison of both calculations cannot be made due to the presence of "nonphysical" steps in the structure studied by Schlüter *et al.*[22]

IV. CONCLUDING REMARKS

We have developed a method to calculate electronic densities of states in stepped semiconductor surfaces. The method, based on the Bethe-Peierls approximation, neglects everything except short-range order. The effects on the density of states of the presence of steps in the surface appears very clearly against the density of states of a planar surface. Since we work in the real-space representation, there is no need of k-space integrations.

Results of our calculations are in very good agreement with ultraviolet-photoemission-spectroscopy data on Si stepped surfaces. In spite of this agreement the calculation can be improved in several ways:

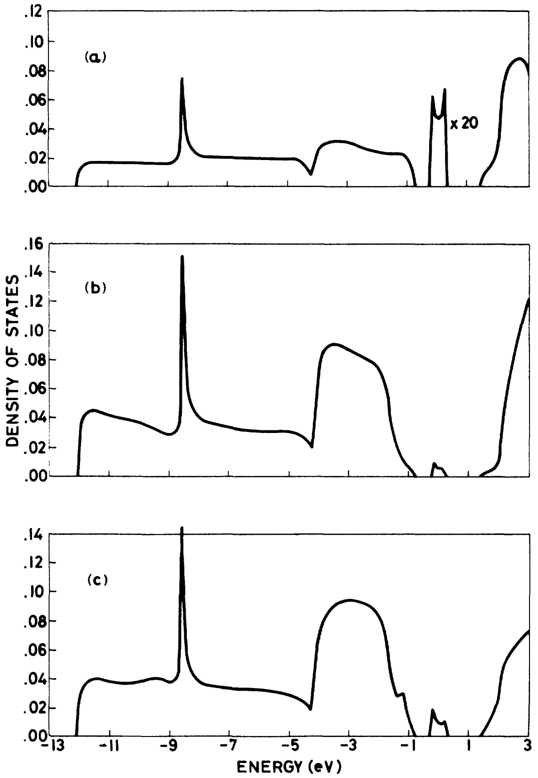

FIG. 12. Local densities of states at orbitals in the atom labeled 4 in Fig. 8. (a) Local density of states corresponding to the orbital labeled 1. (b) Local density of states corresponding to the orbital along the directions labeled 2 and 4. (c) Local density of states corresponding to the direction labeled 3. The solid vertical straight line represents a δ-function contribution to the density of states.

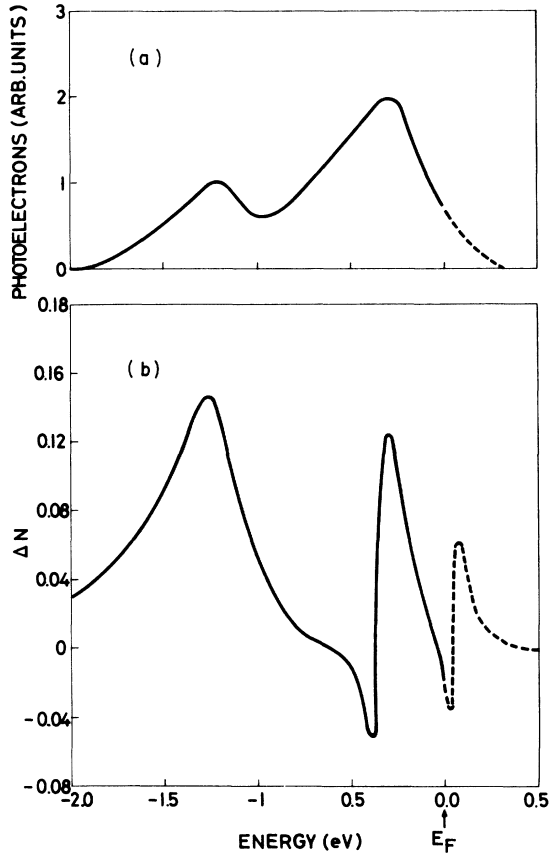

FIG. 13. Difference between the stepped and planar surface density of states. (a) According to ultraviolet-photoemission-spectroscopy data (see Ref. 18). (b) Results of our calculation.

(i) The Hamiltonian only includes nearest-neighbor interactions. It is known that more distant overlaps provide a better description of the conduction band.[14,23] Even more, for a more appropriate description of the electronic structure of group-IV semiconductors, it is necessary to include d electrons.[24]

(ii) Our approximation neglects the effects of the presence of closed rings of bonds. Inclusion of this effect would require studying clusters of atoms.

(iii) We only change the atomic potentials at the surface while keeping fixed the other Hamiltonian parameters. This should be improved with a less parametrized Hamiltonian.

(iv) In our calculation of the surface states we do not include any reconstruction even though experimentally[25] it is known that such reconstruction is present.

(v) In the calculation of electron states at the step we neglect any relaxations, in spite of the fact that such relaxation does exist.[17] This relaxation seems to originate the state at the bottom of the valence band. We have calculated the density of states assuming a relaxation of the step's edge atoms and we obtain a state below the bottom of the valence band without a substantial change of the other density-of-states features.

In spite of the limitations of our model we believe that the obtained results are reliable because the origin of the different features introduced in the density of states by the presence of the step are understood in rather clear physical grounds.

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