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Electronic structures of HgTe and CdTe surfaces and HgTe/CdTe interfaces

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A Green's-function method has been used to study the surface and interface electronic structures of the II-VI compounds HgTe and CdTe. Localized surface and resonance states near the cation-terminated (100) surface of CdTe and the anion-terminated surface of HgTe have been found for the ideal surfaces. The energies and strengths of these surface states are altered by surface perturbations. The bulk states near the surface are drastically modified by the creation of the surface, but the band gaps remain unchanged. Numerical evaluation of the local densities of states at the Γ and J points shows that, at the (100) interface of HgTe/CdTe, the previously observed surface states are no longer present. However, in the interface region, bulk states of one material penetrate some distance into the other material.

I. INTRODUCTION

One of the earliest formulations used in the investigation of surfaces and interfaces was based on the linear combination of atomic orbitals (LCAO) method. Goodwin[1] first applied the LCAO model to study the existence conditions for localized Tamm[2] states in a crystal. He found that these states occur when the diagonal Coulomb integrals and the off-diagonal resonance integrals of the surface are allowed to be different from those of the bulk, for systems of single-level or of *sp*-hybridized atoms. At the same time, Shockley[3] investigated a periodic potential that is terminated at its maximum and found that, under the condition that the bulk bands crossed, surface states exist in the middle of the band gap. Shockley states, as they have come to be known, come into being when the perturbations at the surface are small in comparison to the widths of the allowed energy bands. Koutecky[4] and others[5] generalized Goodwin's model to study the energy and existence conditions of surface states. Electronic interface states were studied within the LCAO method by Davison and Cheng.[6] An exact tight-binding solution for the surface and interface problems of a one-dimensional semiconductor was obtained by Dy and co-workers.[7,8]

Since these early investigations, many other papers have appeared in the literature for the study of surface and interface properties of solids. Kalkstein and Soven (KS) (Ref. 9) introduced a Green's-function (GF) formalism to study the surface electronic properties of semi-infinite crystals. This is a relatively simple but powerful method by which both the bulk and surface properties of a semi-infinite crystal can be studied. The method can be generalized in a straightforward manner to study the electronic properties of an interface formed by joining two semi-infinite crystals. Because of its simplicity and power the method of KS was widely applied in many calculations during the decade following its development.[10-14] For the same reasons we apply this method in this work to investigate surface and interface electronic structures of the pure II-VI compounds CdTe and HgTe.[15,16]

Despite the intense interest in $\mathrm{Hg}_{1-x}\mathrm{Cd}_x\mathrm{Te}$ over the past three decades due to its application in the preparation of infrared detectors, there have been relatively few experimental and theoretical investigations of the surface and interface properties of this system.[17-19] Since the KS method is well suited for the study of the surface properties of a system described by a tight-binding Hamiltonian, we use here a Hamiltonian closely related to that obtained by Hass, Ehrenreich, and Velicky (HEV) (Ref. 20) for HgTe and CdTe in the empirical tight-binding approximation (ETBA) based on the LCAO interpolation scheme of Slater and Koster.[21] In the ETBA the predicted band structures of the pure compounds HgTe and CdTe are matched to experimentally determined band energies.[22]

In Sec. II, we introduce the formalism of KS for the description of the surface properties of II-VI materials along with the extension of the technique to the problem of interfaces of these materials. Section III contains the results of our calculation and a discussion.

II. FORMALISM

In the formalism of Kalkstein and Soven,[9] a pair of semi-infinite crystals is formed by introducing a cleavage plane into an infinite crystal in one crystallographic direction. A GF describing the electronic properties of the semi-infinite systems is derived from the GF of the infinite crystal and a scattering potential representing the cleavage. When combined with a tight-binding formalism in which nearest- and next-nearest-neighbor interactions are included, the scattering potential is relatively easy to calculate making application to realistic systems simple. The Hamiltonian is constructed, following HEV, for HgTe and CdTe using sp^3 basis states and including spin.[20,23] The parameters used are those of Slater and Koster[21] as determined by HEV (Ref. 20) except that, in our case, the values of $Esx(110)$ and $Esx(011)$ are interchanged. This produces band structures[15,16] that are qualitatively similar to those of Bryant which offer improved conduction-band mass.[18] We calculate the GF, G associated with this Hamiltonian by using the defining equation

$$G=(E+i\lambda-H)^{-1}, \tag{1}$$

where H is the Hamiltonian of the infinite unperturbed system. It is understood that G is to be calculated in the limit as the positive imaginary part λ approaches zero. These calculations are performed in k space, utilizing fully the periodicity of the crystal.

For the surface (interface) calculations, since we no longer have translational periodicity along the direction perpendicular to the surface (interface), we cannot use an ordinary k-space representation. Kalkstein and Soven[9] assume periodic structure parallel to the surface and use a representation consisting of states which are localized on planes of atomic sites parallel to the surface and represented by the index n, and of Bloch states reflecting the periodic symmetry within the planes which are represented by the index $\mathbf{k}_{\parallel}$. This is the mixed or Bloch-Wannier representation. We assume the same type of symmetry in the interface system. The Hamiltonian and the GF of the bulk crystal as well as the Hamiltonians of the semi-infinite and interface systems must all be expressed in this mixed representation. The formulas for the semi-infinite system were derived by KS and are the same for us if we reinterpret the algebraic expressions as matrix equations for the sp^3-spin basis states. Note that in this paper we examine the surfaces and interfaces perpendicular to the [100] direction for pure CdTe and HgTe samples. For these compounds, this structure corresponds to an arrangement in which the anions and cations are placed in alternating planes parallel to the surface or interface. For notational simplicity, in the following, a cation-anion pair of planes is given a single layer index n, with the species index ν left to distinguish between the two species (layers).[15,16]

For basis states of the infinite system, KS used states analogous to $|\alpha\sigma\nu\mathbf{k}\rangle$, where $\alpha=s,x,y,z$ indicates the atomic orbital, the spin ($\uparrow,\downarrow$) is represented by σ, $\nu=a$ or c stands for anions or cations, respectively, and $\mathbf{k}$ is the wave vector. Following KS, we write the Bloch-Wannier states for our system as

$$|\alpha\sigma\nu n\mathbf{k}_{\parallel}\rangle=\frac{1}{N_{\perp}}\sum_{\mathbf{k}_{\perp}}e^{-i\mathbf{k}\cdot\mathbf{R}_{n\nu}}|\alpha\sigma\nu\mathbf{k}\rangle, \tag{2}$$

where $\mathbf{R}_{n\nu}$ is the position of the ion sublattice represented by ν on the plane labeled by n, and $\mathbf{k}_{\parallel}$ and $\mathbf{k}_{\perp}$ are the components of $\mathbf{k}$, parallel and perpendicular to the surface (interface) plane, respectively. This basis set reflects the symmetry of the semi-infinite system and is therefore well suited for our purpose. In the following we suppress the $\mathbf{k}_{\parallel}$ index for compactness of notation, as in

$$G(n,n')=\sum_{\alpha\sigma\nu}\sum_{\alpha'\sigma'\nu'}\langle\alpha\sigma\nu n\mathbf{k}_{\parallel}|G|\alpha'\sigma'\nu'n'\mathbf{k}_{\parallel}\rangle \times|\alpha\sigma\nu n\mathbf{k}_{\parallel}\rangle\langle\alpha'\sigma'\nu'n'\mathbf{k}_{\parallel}|, \tag{3}$$

which is the GF submatrix between layer n and layer n'.

From the site-diagonal GF, $G(n,n)$, we may calculate the local density of states

$$\rho_{n\nu}(E)=-(1/\pi)\,\mathrm{Im}\,\mathrm{Tr}_{\nu}G(n,n), \tag{4}$$

where Tr_{ν} indicates that the trace is to be carried out only for the species (layer) given by ν.

The GF of the semi-infinite crystal, G' is found through the application of the Dyson equation,

$$G'=G+GVG'. \tag{5}$$

Besides calculating the matrix elements of the infinite crystal GF, G, we must also find the matrix elements of the scattering potential, V, introduced by the creation of the surface. We label the double layers in the crystal with integers such that the cleavage plane passes between the double layers -1 and 0, and the semi-infinite crystal of interest starts at the zeroth layer and has layer indices $n\geq 0$. Because $G'(n,n')$ is zero for all n and n' less than zero, the only matrix elements of the scattering potential that enter into Eq. (5) in the present model are $V(-1,0)$ and $V(0,-1)$ which express the severing of the interactions across the cleavage plane. We may also include a diagonal term $V(0,0)$, if we wish, to allow for surface perturbations such as relaxation and environmental shifts, into our calculation. These scattering potentials have explicit dependence on $\mathbf{k}_{\parallel}$ and the pair of indices associated with V refer to the double layers involved in the interaction. In terms of the Hamiltonian matrices, the scattering potential matrix is given by

$$V=H'-H, \tag{6}$$

where H' is the Hamiltonian of the semi-infinite crystal. The scattering potential matrix elements describing the breaking of interactions across the cleavage plane are[9]

$$\begin{aligned}V(0,-1)&=-H(0,-1),\\ V(-1,0)&=-H(-1,0),\end{aligned} \tag{7}$$

where, as before, the $\mathbf{k}_{\parallel}$ index has been suppressed for compactness of notation. The matrix element $V(0,0)$ is introduced parametrically to account for the shifts in the atomic levels and hopping interaction at the surface layer.

Explicitly, a general matrix of G' is found from Eq. (5) as

$$\begin{aligned}G'(n,n')=G(n,n')&+[G(n,0)V(0,0)\\&+G(n,-1)V(-1,0)]G'(0,n'),\end{aligned} \tag{8}$$

with n and $n'\geq 0$. To solve this equation, it is first necessary to solve for $G'(0,n')$ which is done by setting n equal to zero in Eq. (8) and solving for the matrix element

$$G'(0,n')=[1-G(0,0)V(0,0)-G(0,-1)V(-1,0)]^{-1}G(0,n') . \qquad (9)$$

To find the general matrix element of G' we need only to substitute Eq. (9) into Eq. (8). To include environmental effects on the surface atoms, we introduce a parameter δ which measures a shift of the surface layer on-site energies. Also, we introduce a parameter d which represents the strength of the interactions between the first two planes of atoms in the semi-infinite crystal relative to the same interactions in the bulk. The parameters δ and d are included in the matrices $V(0,0)$ and $V(-1,-1)$.[15,16]

This model was first extended to the interface between two model semi-infinite one-band crystals by Yaniv.[13] We further extend the technique to real crystals using the sp^3 with spin basis states. The interface is formed between crystal A ($n \leq -1$) and crystal B ($n \geq 0$). In joining the crystals, the interactions between the Te and Cd planes, as well as those between the Te planes, across the interface, are taken to be the same as in the bulk. Since there are no data available for the hopping integrals between Hg and Cd planes we assume them to be equal to the average of the interactions between bulk-crystal (100) Cd planes in CdTe and interactions between bulk-crystal (100) Hg planes in HgTe. The interactions between the A and B sides of the interface are included in the scattering potentials $V'(0,-1)$ and $V'(-1,0)$. To our Green's function we add subscripts α and β which take on the values A and B to indicate the side of the interface involved in the calculations. Once again solving the Dyson equation for the interface GF, g (Ref. 16),

$$g=G'+G'V'g$$

we find the interface GF matrix elements as

$$g_{\alpha\beta}(m,n)=G'_{\alpha}(m,n)\delta_{\alpha\beta}+G'_{B}(m,0)V'(0,-1)g_{A\beta}(-1,n)\delta_{\alpha\beta}+G'_{A}(m,-1)V'(-1,0)g_{B\beta}(0,n)\delta_{\alpha A} , \qquad (10)$$

where

$$g_{AA}(-1,n)=[1-G'_{A}(-1,-1)V(-1,0)G'_{B}(0,0)\times V(0,-1)]^{-1}G'_{A}(-1,n) , \qquad (11a)$$

$$g_{BB}(0,n)=[1-G'_{B}(0,0)V(0,-1)G'_{A}(-1,-1)\times V(-1,0)]^{-1}G'_{B}(0,n) , \qquad (11b)$$

$$g_{BA}(0,n)=G'_{B}(0,0)V(0,-1)g_{AA}(-1,n) , \qquad (11c)$$

$$g_{AB}(-1,n)=G'_{A}(-1,-1)V(-1,0)g_{BB}(0,n) , \qquad (11d)$$

and $\delta_{\alpha\beta}$ is the Kronecker delta. We have assumed a perfect match in the lattice spacing across the interface which is nearly true for HgTe and CdTe with a difference in spacing of only 0.3%.

In the evaluation of the GF of the bulk system a great deal of numerical integration is required. The integrals are evaluated through the use of a Lagrange interpolation scheme in which the time to calculate the band structures is reduced by evaluating them exactly at only a few points in k space and interpolating for the intermediate values.[24] Accuracy is ensured through sampling the functions at a sufficient number of points. All calculations are performed with a small positive imaginary component in the energy and the final results at the real energy axis are evaluated through the use of the analytic continuation procedure of Hass, Velicky, and Ehrenreich.[25]

One quite useful feature of our calculation is that the evaluation of the GF's of the semi-infinite crystal and the interface requires much less computational effort than the evaluation of the infinite crystal GF.[16] As a result of this speed, we are able to consider several values of the environmental shift and surface–nearest-neighbor interaction. In order to observe the effects of the variation of these parameters on the localized states we examine the local densities of states (LDOS) at various values of the parameters for a few CdTe and HgTe surfaces and interfaces. These LDOS are evaluated at fixed values of $\mathbf{k}_{\parallel}$ so that we may find the positions of the localized state bands in the surface Brillouin zone. For details of the evaluation of the matrix elements of the infinite crystal GF and those of the scattering potentials required for our calculation, one is referred to Refs. 15 and 16.

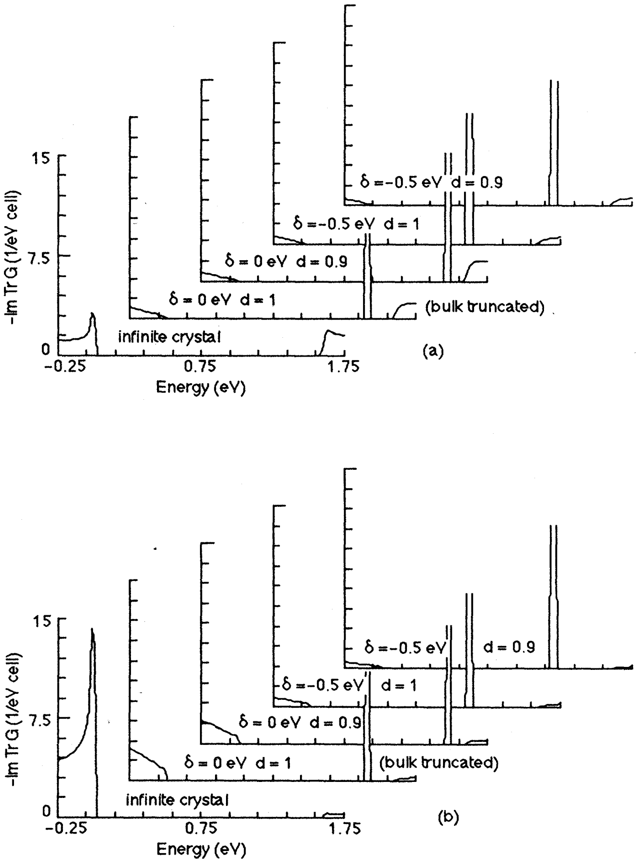

FIG. 1. Dependence of the LDOS on the parameters δ and d as compared to the infinite crystal for (a) the cation surface layer and (b) the first interior anion layer at Γ ($\mathbf{k}_{\parallel}=0$) for CdTe cation-terminated (100) surface.

III. RESULTS AND DISCUSSION

Once the matrix elements of the infinite crystal GF and the relevant scattering potentials are specified, one can calculate the matrix elements of the GF of the semi-infinite sample and that of the sample with the interface using Eqs. (8) and (10), respectively. One can further calculate the LDOS at various layers using an equation of the type of Eq. (4). In this paper we present the LDOS calculated at the symmetry points Γ and J and at energies near the valence- and the conduction-band edges of the sample where the principal band gaps occur.

In Figs. 1 and 2 we plot the surface LDOS at the Γ point for various combinations of the environmental shift parameter δ and the geometric shift parameter (relaxation parameter) d for CdTe cation-terminated and HgTe anion-terminated crystals, respectively. We begin by noting, in Fig. 1, the existence of a localized surface state (bound state) which is the sharp structure that appears in the LDOS within the band gap of the CdTe, whether or not there is a surface perturbation. The ideal cation-truncated (100) surface of CdTe has a surface state at Γ with energy lying at $E = 0.6$ eV above the top of the valence band. We also see that the bulk densities of states are modified as a result of the introduction of a surface but the band gap of CdTe remains unchanged. We note that the position of the bound state is sensitive to

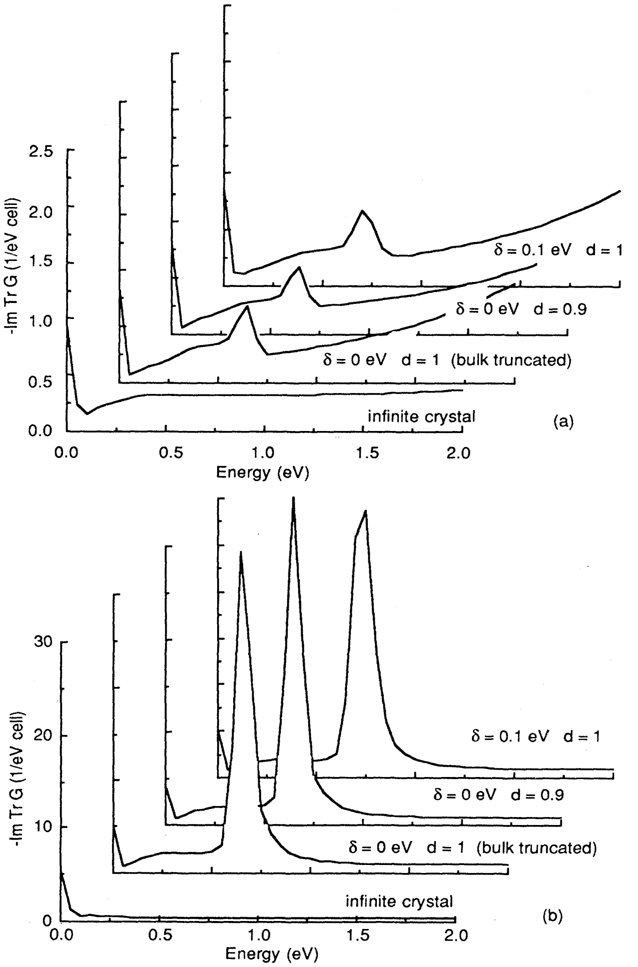

FIG. 2. Dependence of the LDOS on the parameters δ and d as compared to the infinite crystal for (a) the anion surface layer and (b) the first interior cation layer at Γ ($\mathbf{k}_{\parallel}=0$) for HgTe cation-terminated (100) surface.

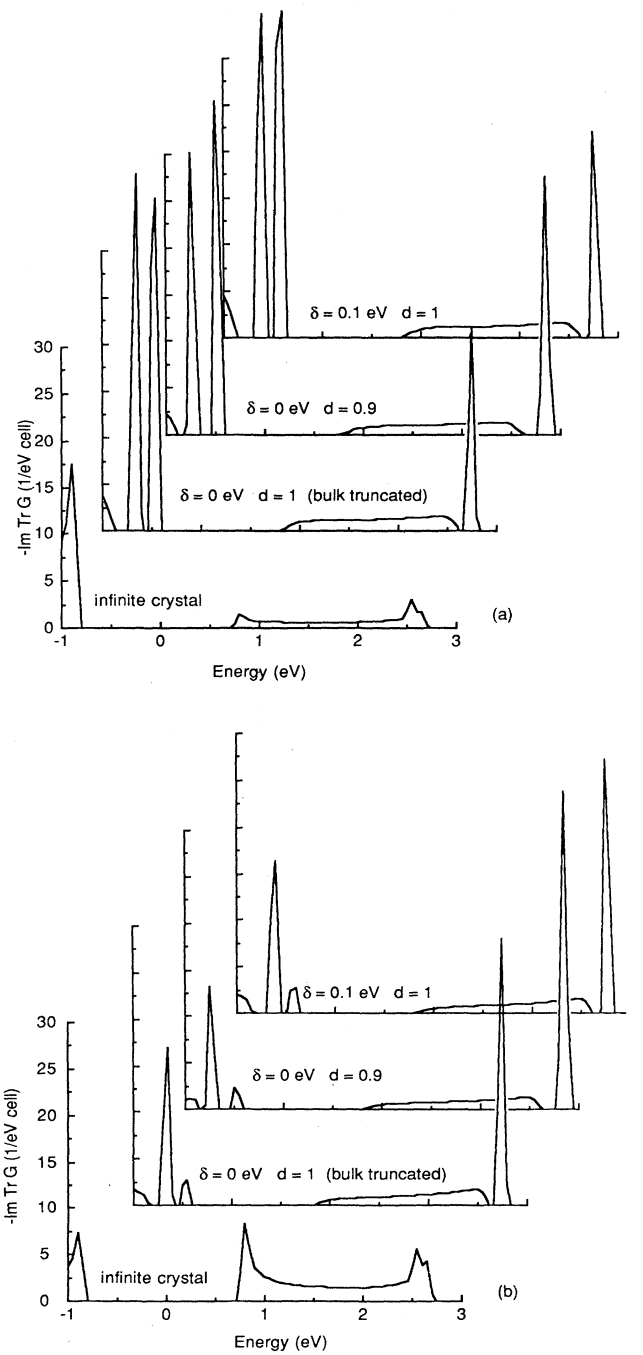

FIG. 3. Dependence of the LDOS on the parameters δ and d as compared to the infinite crystal for (a) the anion surface layer and (b) the first interior cation layer at J [$\mathbf{k}_{\parallel}=\pi/a(\sqrt{2},\sqrt{2})$] for HgTe anion-terminated (100) surface.

variations in both d and δ. In Fig. 2, we notice that the surface has again introduced a marked change in the LDOS of HgTe. A resonance state appears in the form of a spike inside the conduction band of semimetal HgTe. The contribution of this resonance to the LDOS is strongest for anion layers indicating that anion states are the most likely constituents of this state. Similar surface states have been calculated by Bryant[18] for the special case where no surface perturbations exist.

The surface states calculated for the HgTe at the J point where there exists a gap are shown in Fig. 3. These states exhibit the same dependence on the interactions that was seen at the Γ point. Here instead of a single peak we see a pair of bound states just above the valence band within the band gap. Also above the conduction band there is a bound state that was not observed for the Γ point. Anions contribute more strongly to the bound states inside the band gap while the cation contribution is stronger to the bound state above the conduction band. Also notice that the bulk states are strongly modified by the introduction of the surface and that the band gaps are not altered by the surface.

Our calculation of the layer dependence of the surface states shows that these states become progressively less significant as we examine deeper inside the crystal indicating these states are indeed localized bound states. The bulk LDOS in the deeper layers, on the other hand, start resembling the infinite crystal LDOS.

As mentioned before, the interface calculations have been performed assuming no lattice mismatch in the crystal structures of the HgTe and CdTe compounds, thus neglecting all strains that may be present at the interface. The parameters chosen for our calculation also do not allow for valence-band offset. With these assumptions, dramatic effects are seen at the interface of HgTe and CdTe as shown in Figs. 4 and 5, where the LDOS in the CdTe side of the interface are presented at Γ and J points, respectively. The most obvious effect is the lack of localized states that were previously seen at the free surfaces of these materials. Instead, we find that, close to the interface, the bulk states of HgTe that lie in the region between 0 and 1.6 eV appear in the band gap of

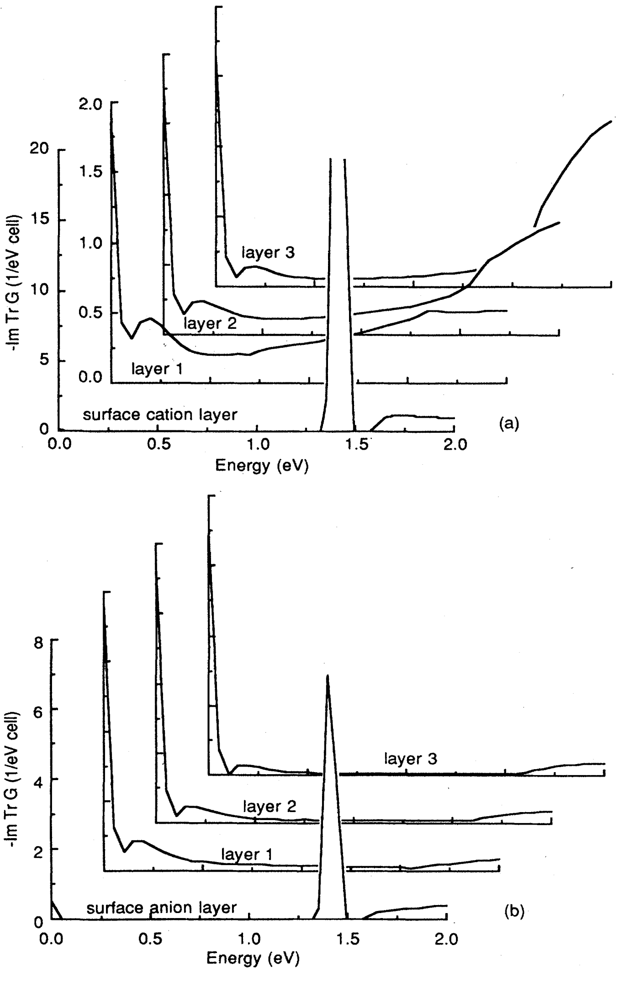

FIG. 4. Comparison of the surface LDOS of the cation-terminated (100) surface of CdTe with the LDOS plotted (a) at successive cation layers and (b) anion layers for the CdTe side of the (100) interface CdTe/HgTe at Γ.

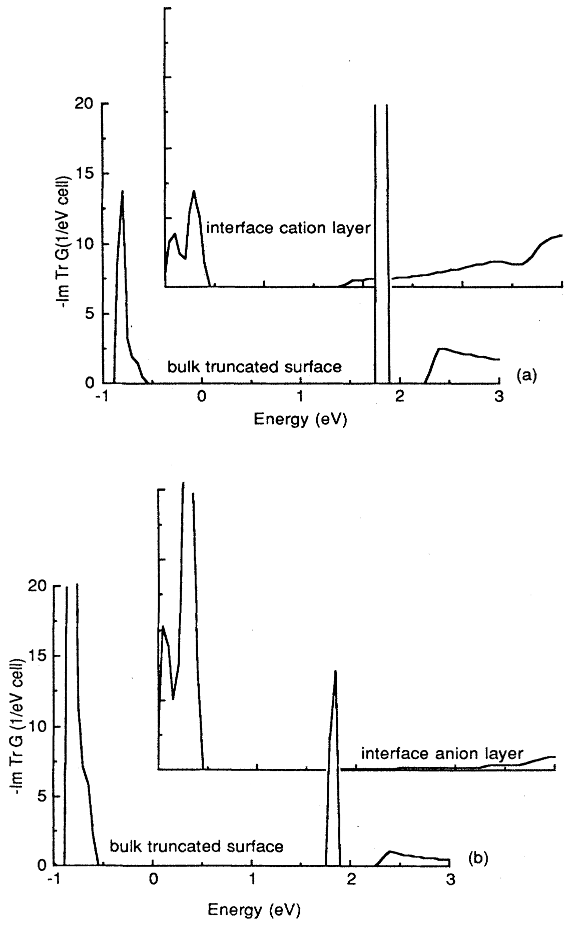

FIG. 5. Comparison of the surface LDOS of the cation-terminated (100) surface of CdTe with the LDOS plotted (a) at first cation layer at the interface and (b) the first interior anion layer for the CdTe side of the (100) interface CdTe/HgTe at J.

CdTe at the Γ point. These states in the CdTe gap become less significant at layers further from the interface while at the same time the LDOS in the energy ranges of the conduction and valence bands of CdTe increase in strength. Thus we have a narrowing of the gap of CdTe in a limited region near the interface which allows conduction electrons to penetrate into the CdTe from the HgTe over a short distance. In Fig. 5, we explicitly see how the gap at the CdTe layers is reduced with respect to pure CdTe at J. Calculation of the LDOS in the HgTe side of the interface shows similar effects.

The above results describe how the LDOS change from the bulk to the surface and then from the surface to the interface. While the bulk and the interface results can be considered realistic, the surface results may not be, since the surface reconstruction has not been included in the calculation. Recent experiments[17,26–28] and a structural theory[29] indicate that the surfaces of CdTe and some other II-VI compounds undergo reconstructions similar to those on the surfaces of III-V compounds. However, similar measurements are yet to be made on HgTe surfaces and CdTe/HgTe interfaces. Our calculations indicate that changes in the electronic structure in the form of environmental shifts at the surface lead to only minor changes in the localized surface and the bulk LDOS. Whether a surface reconstruction will result in substantial modification of these states is yet to be determined.

In conclusion, we have described in this paper how one can incorporate the GF method of KS to calculate the surface and interface structures of II-VI compounds without having to deal with the artificial super-cell approximation. Our calculation shows that drastic changes in the LDOS can occur because of creation of surfaces and interfaces. Localized surface or resonance states appear above the top of the valence band, and the effects of the surface on the LDOS persist at several layers inside the bulk. At the interface, there are no localized states but the bulklike states related to one material penetrate into several layers inside the other material resulting in narrowing of band gaps close to the interface for the wide band-gap material. At present there are no systematic experimental data available for comparison with our conclusions.

Finally, even though we have not included all aspects necessary for a complete description of the surfaces and interfaces, our work can be considered to be the first step toward the understanding of the surface and interface electronic structures of the II-VI compounds. To our knowledge, the results presented here are new for the interface and more general than any previous surface calculations on the II-VI compounds. Since the method is flexible, it will be possible to incorporate realistic structural models dealing with the surface reconstructions, when they become available, to calculate more realistic electronic properties of such surfaces and interfaces.

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