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Adsorption of zinc on cadmium telluride and mercury telluride surfaces

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Modifications of the surface properties of cadmium and mercury telluride due to the adsorption of zinc atoms are investigated. The bulk band structure is obtained by parametrizing the matrix elements in an empirical tight-binding Hamiltonian. A tellurium-terminated (111) surface is formed by introducing an infinite repulsive potential localized within a layer of cations. The adsorption of a Zn atom at a centered site is studied. The adsorption properties calculated are (i) the change in density of states, (ii) charge densities, and (iii) binding energies as functions of the adsorption parameters.

I. INTRODUCTION

Both cadmium telluride and mercury telluride II-VI compounds have attracted considerable interest over the past decade particularly with the development of such photonic devices as injection lasers, light-emitting diodes, photodetectors, nuclear detectors, and solar cells. The compounds CdTe and HgTe can be mixed to give the single-phase disordered alloy $Hg_{1-x}Cd_xTe$. There is a growing demand for high-density infrared detector arrays using this substitutional alloy with its high electron mobility because the fundamental optical absorption edge can be varied as a function of composition x over almost the entire infrared spectrum.

The surface properties of II-VI semiconductors are of interest in the context of device fabrication and characterization. Since the fabrication of well-characterized surfaces of these semiconductors is very recent, the problem is yet to attract wide theoretical and experimental interest. The investigation of CdTe-HgTe interfaces was carried out recently by Schick, Bose, and Chen.[1] They started from realistic bulk bands, created clean surfaces, and then allowed two (111) surfaces to couple.

In the present work the adsorption properties due to the adsorption of zinc on tellurium-terminated (111) surfaces of CdTe and HgTe has been investigated. Adsorption on CdTe and HgTe has a number of interesting properties due to the unique features of these semiconductors. Their energy bands have considerable s and p orbital mixing away from the center of the Brillouin zone, and the binding of the adatom to the surface will thus depend critically on the position of its atomic energy levels relative to the semiconductor bands. When all other parameters remain constant, an adsorbed atom with an electron in the valence s state should bind more efficiently if the atomic s state is nearly degenerate in energy with the bottom of the conduction band with which it shares s-like symmetry, than if it is lined up with the edge of the valence band where the symmetry is nearly p-like.

The adsorption of an atom may cause a new localized state to be formed which can encourage or deter adsorption of additional atoms. By fabricating samples with a range of dopant concentrations, the Fermi level can be swept through the energy level of the adsorbed atomic state. Systematic trends for such adsorption characteristics as heat of adsorption and charge transfer from the surface to atom are of particular interest.

The effects of the adsorption of model single-level atoms on (111) surfaces of CdTe and HgTe and their alloys were studied by Kreuzer, Neilson, and Szymański.[2] They used the Kane model[3] to describe the bulk bands.

This is the first calculation using surfaces obtained from realistic empirical tight-binding bulk bands to study the effect of a specific adsorbate atom (Zn) on CdTe and HgTe. We have investigated the effects of adsorption on the surface density of states as well as the electron occupancy and binding energy of the adatom as a function of the electron concentration of the bulk.

II. THEORY

A. Bulk bands

CdTe and HgTe are II-VI semiconductors with a unit cell containing one anion and one cation. They form tetrahedrally directed covalent bonds from the hybridized s and p atomic orbitals. The eight valence electrons are

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distributed among the one s and three p atomic orbitals. We label the type of atom by η (where $\eta = a$ for the anion and $\eta = c$ for the cation), and the s, p_x, p_y, p_z orbitals by β (with $\beta = s, x, y, z$). Each electron spin is labeled by σ (where $\sigma = \uparrow, \downarrow$). The orthogonalized Löwdin functions[4] $\psi_\mu(\mathbf{r} - \mathbf{R}_j)$ can be constructed from the atomic orbitals in the elementary cell $\mathbf{R}_j$. The label μ stands collectively for (β, σ, η).

The orthonormal set of wave functions $\chi_{\mu\mathbf{k}}(\mathbf{r})$ for an electron in a crystal can be expressed as a linear combination of the Löwdin functions, each localized in a different elementary cell,

$$\chi_{\mu\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N_3}} \sum_j e^{i\mathbf{k}\cdot(\mathbf{R}_j+\boldsymbol{\tau}_\eta)} \psi_\mu(\mathbf{r} - \mathbf{R}_j - \boldsymbol{\tau}_\eta). \tag{1}$$

N_3 is the total number of lattice points in the bulk. The vector $\boldsymbol{\tau}_\eta$ specifies the position of the anion or cation η relative to the origin of the cell $\mathbf{R}_j$. We take $\boldsymbol{\tau}_\eta = \delta_{\eta,c}\,(r_0/4)(1,1,1)$, where r_0 is the cubic lattice constant (so that the anion is at the origin).

Relativistic corrections are important for these semiconductors[5] and have to be included in the Hamiltonian which we write for the bulk system as

$$H^B = h + h^s. \tag{2}$$

h includes the kinetic energy, the potential energy, and the spin-independent relativistic corrections, while h^s contains the spin-orbit interactions.

The matrix elements of h are given by

$$\begin{aligned} E'_{\mu\mathbf{k},\mu'\mathbf{k}'} &= \int d^3\mathbf{r}\, \chi^*_{\mu\mathbf{k}}(\mathbf{r})\, h\, \chi_{\mu'\mathbf{k}'}(\mathbf{r}) \\ &= \delta_{\sigma,\sigma'}\delta_{\mathbf{k},\mathbf{k}'} \sum_{lmn} e^{i\mathbf{k}\cdot(\mathbf{R}_j+\boldsymbol{\tau}_{\eta'}-\boldsymbol{\tau}_\eta)}\, E'_{a\eta,\,a'\eta'}(l,m,n)\,, \end{aligned} \tag{3}$$

where the $E'_{a\eta,\,a'\eta'}(l,m,n)$ are the Slater-Koster parameters.[6] We can write $(\mathbf{R}_j + \boldsymbol{\tau}_{\eta'} - \boldsymbol{\tau}_\eta) = (a/4)(l\mathbf{i} + m\mathbf{j} + n\mathbf{k})$ where l, m, and n are integers and $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are unit vectors along the Cartesian directions.

Since the spin-orbit interactions are short ranged, only interactions on the one atom need be considered, and h^s is taken to be that for the isolated atom. Its matrix elements are only nonzero for elements linking different p orbitals on the same atom. We represent this by the two parameters Λ_η,

$$< x, \sigma, \boldsymbol{\tau}_\eta \mid h^s \mid z, -\sigma, \boldsymbol{\tau}_\eta > \equiv \Lambda_\eta. \tag{4}$$

Combining the results of Eqs. (3) and (4) we obtain the bulk Hamiltonian H^B in the form of the 16×16 matrix $< \mu, \mathbf{k} \mid H^B \mid \mu', \mathbf{k} >$. This matrix has eleven adjustable parameters for first-nearest-neighbor interactions and twenty-five for second. These are selected to fit the energy eigenvalues $E_0^n(\mathbf{k})$ to the observed band structure for the bulk material.[7] The eigenvalues $E_0^n(\mathbf{k})$ and eigenvectors $C_\mu^n(\mathbf{k})$ of H^B are obtained by diagonalizing $< \mu, \mathbf{k} \mid H^B \mid \mu', \mathbf{k} >$. The Bloch eigenfunctions $\psi^0_{n\mathbf{k}}(\mathbf{r})$ are given by

$$\psi^0_{n\mathbf{k}}(\mathbf{r}) = \sum_\mu C_\mu^n(\mathbf{k}) \chi_{\mu\mathbf{k}}(\mathbf{r}). \tag{5}$$

Figure 1 shows our results for the bulk bands of CdTe and HgTe.

B. Surface properties

We generate the (111) surfaces of CdTe and HgTe using the Green-function formalism which Pollmann and Pantelides[8] developed for free surfaces of tetrahedral semiconductors. In this approach, the crystal is decou-

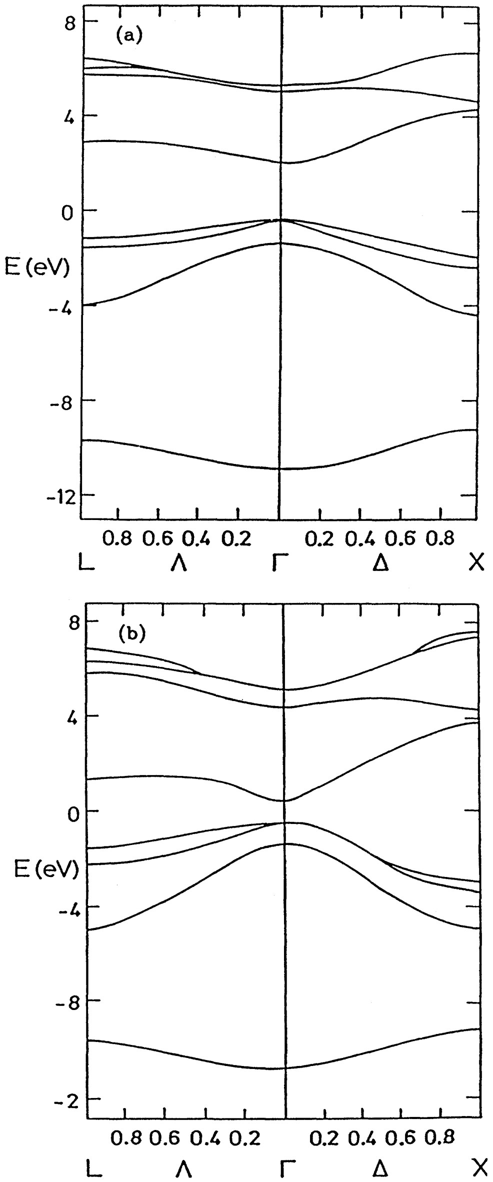

FIG. 1. Bulk energy bands along the Δ and Λ directions of the Brillouin zone for nearest-neighbor interactions. (a) CdTe. (b) HgTe.

pled into two semi-infinite solids with cation-terminated surfaces by removing one layer of anions from the bulk crystal. There are several advantages in following this procedure. Compared with the slab method,[9] the matrices employed in the present approach are much smaller. Since semi-infinite solids are used, the band continua are described by continuous functions instead of by a set of discrete states. In contrast to the method in which the surfaces are created by cutting bonds,[10] the electronic structure of the unrelaxed surfaces are contained entirely in the Green function of the perfect infinite solid when the surfaces are created by removing a layer of atoms. This preserves the bulk properties so that the subsequent changes are produced directly without having to subtract large quantities. In this approach the Green-function matrix of localized surface states is automatically Hermitian.

We introduce a mixed plane-wave and Bloch-Löwdin representation, writing $\mathbf{R}_j$ in the form $\mathbf{R}_j = \mathbf{R}_{\|j} + m\mathbf{d}$ and $\boldsymbol{\tau}_\eta = \boldsymbol{\tau}_{\|\eta} + \boldsymbol{\tau}_{\perp\eta}$. The integer m labels the different layers parallel to the surface each separated by the displacement vector $\mathbf{d}$. The vector $\mathbf{R}_{\|j}$ is the two-dimensional Bravais lattice vector parallel to the surface.

For the surface basis set we use the layer orbitals $\mid \mu, m, \mathbf{k}_\| >$ which are defined in terms of the Löwdin orbitals for the particular layer $\psi_\mu(\mathbf{r} - \mathbf{R}_j)$,

$$|\mu, m, \mathbf{k}_\| >= \frac{1}{\sqrt{N_2}} {\sum_j}' e^{i\mathbf{k}_\| \cdot (\mathbf{R}_{\|j} + \boldsymbol{\tau}_{\|\eta})} \psi_\mu(\mathbf{r} - \mathbf{R}_j - \boldsymbol{\tau}_\eta). \tag{6}$$

The restricted sum is over cells in the surface layer, N_2 is the total number of lattice points on the surface, and $\mathbf{k}_\|$ is the component of $\mathbf{k}$ parallel to the surface.

In this basis the Green function for the bulk system is

$$G^B_{\mu m;\mu' m'}(\mathbf{k}_\|, E) = \sum_{n,k_z} \frac{< \mu, m, \mathbf{k}_\| \,|\, \psi^0_{n\mathbf{k}} >< \psi^0_{n\mathbf{k}} \,|\, \mu', m', \mathbf{k}'_\| >}{E - E^n_0(\mathbf{k}) + i\varepsilon}. \tag{7}$$

The effect of the surface inhomogeneity is represented as a perturbation V^S which is localized in the surface plane. For nearest-neighbor coupling, an anion-terminated (111) surface can be created by "removing" a single layer of cations. This decouples the bulk solid into two noninteracting semi-infinite solids. We accomplish this here by setting the diagonal matrix elements for the particular cation layer equal to a constant w, and we then allow w to go to infinity. This has the effect of decoupling the orbitals in this layer from the rest of the system, the equivalent of introducing a "planar vacancy." We define the potential V^S which acts only on the $m = 0$ layer of cations:

$$< \mu, m, \mathbf{k}_\| \,|V^S \,|\, \mu', m', \mathbf{k}'_\| > = \lim_{w \to \infty} w \delta_{m,0} \delta_{m,m'} \delta_{\eta,c} \delta_{\mu,\mu'} \delta_{\mathbf{k}_\|,\mathbf{k}'_\|}. \tag{8}$$

Along the surface plane the potential V^S has the periodicity of the crystal.

The Green function $G^S(E)$ of the crystal in the presence of the surface can then be obtained from the Dyson equation. Its solution can be written as

$$G^S_{\mu m;\mu' m'}(\mathbf{k}_\|, E) = \sum_{\beta\sigma;\beta'\sigma'} G^B_{\mu m;\nu 0}(\mathbf{k}_\|, E) \times [G^B(\mathbf{k}_\|, E)]^{-1}{}_{\nu 0;\nu' 0} G^B_{\nu' 0;\mu' m'}(\mathbf{k}_\|, E). \tag{9}$$

For brevity we have introduced the collective indices $\nu = (\beta, \sigma, c)$ and $\nu' = (\beta', \sigma', c)$, that is, with η fixed as c.

The condition for the existence of discrete surface states within the band gaps is the vanishing of the determinant

$$D^S(E) \equiv \det[1 - G^B(E)V^S]. \tag{10}$$

In the limit $w \to \infty$ this condition simplifies to

$$D^S_1(E) \equiv \det[G^B_{\nu 0;\nu' 0}(\mathbf{k}_\|, E)] = 0. \tag{11}$$

The total density of states of the perturbed crystal is[11]

$$N(E) = -\frac{1}{\pi} \mathrm{Im}(\mathrm{Tr}\{[E - (H^B + V^S) + i\varepsilon]^{-1}\}) \tag{12}$$

and the change in $N(E)$ due to the creation of the surface is

$$\Delta N(E) = -\frac{1}{\pi} \frac{d}{dE} \left(\tan^{-1} \frac{\mathrm{Im} D^S(E)}{\mathrm{Re} D^S(E)} \right). \tag{13}$$

In our case we may evaluate this by replacing $D^S(E)$ with $D^S_1(E)$ [see Eq. (11)].

The change in density of states is often expressed in terms of a phase shift $\delta(E)$,

$$\Delta N(E) = -\frac{1}{\pi} \frac{d\delta(E)}{dE}. \tag{14}$$

The phase shift $\delta(E)$ goes through an odd multiple of $\pi/2$ each time the energy satisfies the condition $\mathrm{Re} D^S(E) = 0$ for some $E = E_0$. Expanding around E_0, the change in the density of states for energies near a localized surface state can be written as

$$\Delta N(E) = \frac{1}{2\pi} \frac{\Gamma}{(E - E_0)^2 + \Gamma^2/4}. \tag{15}$$

This expression is of the characteristic Breit-Wigner form. The half-width Γ is given by

$$\Gamma = 2\,\mathrm{Im} D^S_1(E_0) \Big/ \left(\frac{d}{dE} \mathrm{Re} D^S_1(E_0) \right). \tag{16}$$

Denoting a particular anion site in the surface layer by the index i, the Green function $G^S_{\lambda i,\lambda' i'}(E)$ is defined as

$$G^S_{\lambda i,\lambda' i'}(E) = \frac{1}{\sqrt{N_2}} \sum_{\mathbf{k}_\|} e^{i\mathbf{k}_\| \cdot (\mathbf{R}_{\|i} - \mathbf{R}_{\|i'})} G^S_{\lambda\lambda'}(\mathbf{k}_\|, E), \tag{17}$$

where the collective index $\lambda = (\beta, \sigma, a, 0)$ is restricted to the surface layer.

C. Interaction of adsorbed atom with surface

We now consider the adsorption of a Zn atom on a Te-terminated (111) surface of CdTe or HgTe. The Zn atom could be sited in the bridge position (see Fig. 2), coupling to three Te atoms and leaving the Zn with a single dangling bond, or it could be located in the atop position directly above a Te atom, in which case it would couple to the dangling bond of a single Te atom in the surface layer, leaving the Zn with three dangling bonds. We assume for this calculation that the Zn is in the bridge position since this should be the lower energy site.

The total Green function $G^{AS}(E)$ for this system is the solution of the Dyson equation,

$$G^{AS}(E) = G^{(0)AS}(E) + G^{(0)AS}(E)\, V^{AS}\, G^{AS}(E), \tag{18}$$

where V^{AS} is the interaction between the Zn atom and the surface, and $G^{(0)AS}(E)$ can be represented by a block diagonal matrix,

$$G^{(0)AS}(E) = \begin{bmatrix} G^{A}_{\alpha\alpha'}(E) & 0 \\ 0 & G^{S}_{\lambda i,\lambda' i'}(E) \end{bmatrix} \cdot \tag{19}$$

$G^{S}_{\lambda i,\lambda' i'}(E)$ is the site-specific Green function given in Eq. (17), with i, $i' = 1,2,3$ labeling the three Te atoms coupled to the Zn atom. $G^{A}_{\alpha\alpha'}(E)$ is a 4×4 matrix representing the Green function for the valence states of the Zn atom. The labels $\alpha = s, x, y, z$ denote the s, p_x, p_y, p_z orbitals of the Zn atom.

The interaction V^{AS} can be written as

$$V^{AS} = \begin{bmatrix} 0 & V_{\alpha,\lambda 1} & V_{\alpha,\lambda 2} & V_{\alpha,\lambda 3} \\ V_{\lambda 1,\alpha} & 0 & 0 & 0 \\ V_{\lambda 2,\alpha} & 0 & 0 & 0 \\ V_{\lambda 3,\alpha} & 0 & 0 & 0 \end{bmatrix} \cdot \tag{20}$$

The submatrices $V_{\alpha,\lambda i}$ couple the atomic orbitals α of the Zn atom to the s and p atomic orbitals λ of the ith Te atom:

$$V_{\alpha,\lambda i} = \begin{bmatrix} V_{ss} & V_{sx} & V_{sy} & V_{sz} \\ -V_{sx} & V_{xx} & V_{xy} & V_{xz} \\ -V_{sy} & V_{yx} & V_{yy} & V_{yz} \\ -V_{sz} & V_{zx} & V_{zy} & V_{zz} \end{bmatrix} \cdot \tag{21}$$

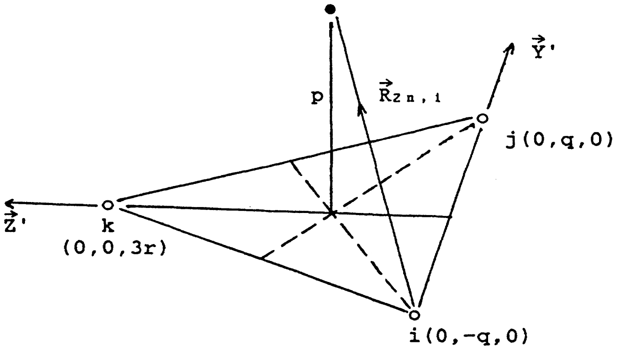

FIG. 2. Zn adatom above the center of three Te atoms in the (111) surface plane of CdTe or HgTe.

In this notation V_{sx} represents the coupling of an s orbital of the Zn atom with a p_x orbital of the Te atom, and so on.

The coupling parameters can be written in Slater-Koster[6] form in which the atomic wave functions are expressed as a sum of functions which are space quantized with respect to an axis formed by the vector joining the two atoms:

$$\begin{aligned} &V_{ss} = V_{ss\sigma}, \quad V_{sx} = l_i\, V_{sp\sigma}, \\ &V_{xx} = l_i^2\, V_{pp\sigma} + (1 - l_i^2) V_{pp\pi}, \\ &V_{xy} = l_i m_i (V_{pp\sigma} - V_{pp\pi}). \end{aligned} \tag{22}$$

The remaining terms can be obtained by cyclic permutation. l_i, m_i, and n_i are the directional cosines of the position vector of the Zn atom with respect to the ith substrate Te atom, $\mathbf{R}_{zn,i}$:

$$\mathbf{R}_{zn,i} = (p\mathbf{X}', q\mathbf{Y}', r\mathbf{Z}'), \tag{23}$$

where

$$p = r_0\sqrt{(d_a/r_0)^2 - 1/6},$$
$$q = r_0/(2\sqrt{2}), \quad r = r_0/(2\sqrt{6}).$$

Once V^{AS} has been specified, Eq. (18) can be solved for the full Green function $G^{AS}(E)$. The change in density of states due to the adsorption is then given by

$$\Delta\rho^{AS}(E) = -\frac{1}{\pi}\mathrm{Im}\{\mathrm{Tr}[G^{AS}(E) - G^{(0)AS}(E)]\}. \tag{24}$$

In our formalism the adatom is present in the system even before it is coupled to the surface and $\Delta\rho^{AS}(E)$ is the change in the density of states when the coupling is switched on. Experiments measure changes in the density of states between the chemisorbed system and the clean substrate without the Zn atom. This is given by

$$\overline{\Delta\rho}(E) = \Delta\rho^{AS}(E) + \frac{-1}{\pi}\mathrm{Im}\{\mathrm{Tr}[G^{A}(E)]\}. \tag{25}$$

The binding energy E_b of the Zn atom to the surface is

$$E_b = \int_{-\infty}^{E_F} dE\,(E - E_F)\overline{\Delta\rho}(E), \tag{26}$$

where E_F is the Fermi energy.

When the adatom-surface coupling is not too strong it is convenient[2] to approximately represent the density of states on the adatom $\rho^{A}(E)$ separately from changes in the density of states on the substrate. We define

$$\rho^{A}(E) = -\frac{1}{\pi}\mathrm{Im}\{\mathrm{Tr}'[G^{AS}(E)]\}. \tag{27}$$

The restricted trace Tr′ sums over only the first four diagonal matrix elements which correspond to the adatom states in the uncoupled case. For weak coupling $\rho^{A}(E)$ and $\overline{\Delta\rho}(E)$ have essentially the same broadened peaks centered at the unperturbed atomic levels of the Zn. This corresponds to the addition of perturbed Zn atomic orbitals to the system. In this case the occupation number of the adatom states n_A is approximately given by[2]

$$n_A \approx \tfrac{1}{8}\int_{-\infty}^{E_F} dE\, \rho^A(E). \tag{28}$$

III. RESULTS

The strength of the coupling between the adatom and the Te atom V^{AS} [see Eqs. (20) and (22)] can be estimated using the method of Froyen and Harrison:[12]

$$V_{ss\sigma} = \frac{\hbar^2}{md^2}\eta_{ss\sigma}, \quad V_{sp\sigma} = \frac{\hbar^2}{md^2}\eta_{sp\sigma},$$
$$V_{pp\sigma} = \frac{\hbar^2}{md^2}\eta_{pp\sigma}, \quad V_{pp\pi} = \frac{\hbar^2}{md^2}\eta_{pp\pi}. \tag{29}$$

d is the distance between the Zn and Te atoms, which we took equal to its value for bulk ZnTe (2.65 Å). The Zn atom is thus taken to be $0.023r_0$ from the Te surfaces for CdTe, and $0.044r_0$ for HgTe. The η's are dimensionless universal constants:[13] $\eta_{ss\sigma} = -1.40$, $\eta_{sp\sigma} = 1.84$, $\eta_{pp\sigma} = 3.24$, $\eta_{pp\pi} = -0.81$.

We must specify the Green function $G^A_{\alpha\alpha'}(E)$ for the Zn atom before it couples to the surface. If spin-orbit interactions within the adatom are neglected, then $G^A_{\alpha\alpha'}(E)$ is diagonal,

$$G^A_{\alpha\alpha'}(E) = \frac{\delta_{\alpha,\alpha'}}{E - E_\alpha + i\varepsilon}. \tag{30}$$

We set the orbital energies E_α equal to the diagonal tight-binding parameters for ZnTe, $E_s = 0.29$ eV and $E_x = E_y = E_z = 5.31$ eV.[13]

We can now solve the Dyson equation [Eq. (18)]. The corresponding changes in the density of states $\Delta\rho(E)$ in going from the clean substrate to the adsorbed system are shown in Fig. 3.

In Fig. 3 we see that the Zn atomic p level at $E_p = 5.31$ eV splits into two peaks at 5.3 and 6.8 eV for the Te surface of CdTe, and at 5.3 and 6.0 eV for HgTe. The s level at $E_s = 0.29$ eV also splits into two peaks at energies -2.5 and 1.5 eV for CdTe, and at -3.0 and 1.1 eV for HgTe. The peaks correspond to the bonding and antibonding split-off states and are similar to the back-bond s state and dangling-bond surface state of Cd- or Hg-terminated surfaces. The peak-dip structure around -9 eV can be identified with a shift in the back-bond anion s state due to the increased binding strength at the surface.

The interpretation of these results is that the Zn atom forms back bonds with the dangling bond of each of the three substrate Te atoms so that the Te dangling-bond states no longer exist. The remaining sp^3 orbital of the Zn atom which is perpendicular to the surface gives rise to a dangling-bond surface state in the antibonding conduction bands. This situation is similar to the creation of a cation-terminated surface where one sp^3 orbital per unit cell is broken. The dangling-bond state of the Cd- or Hg-terminated (111) surface is in the band gap whereas for Zn this state appears in the conduction band because of the more ionic nature of the Zn—Te bond.

In Fig. 4(a) we show n_A, the occupation number (per state) for the Zn atom on CdTe, as a function of the Fermi energy E_F. When E_F crosses the antibonding s state centered around $E = 1.5$ eV the occupation number on the Zn atom n_A increases from 0.12 to 0.25 (corresponding to a jump from about one to two electrons).

Figure 4(b) shows the binding energy E_b of Zn on CdTe as a function of E_F. This increases monotonically with E_F as the occupied s states on the adatom move down relative to the Fermi energy.

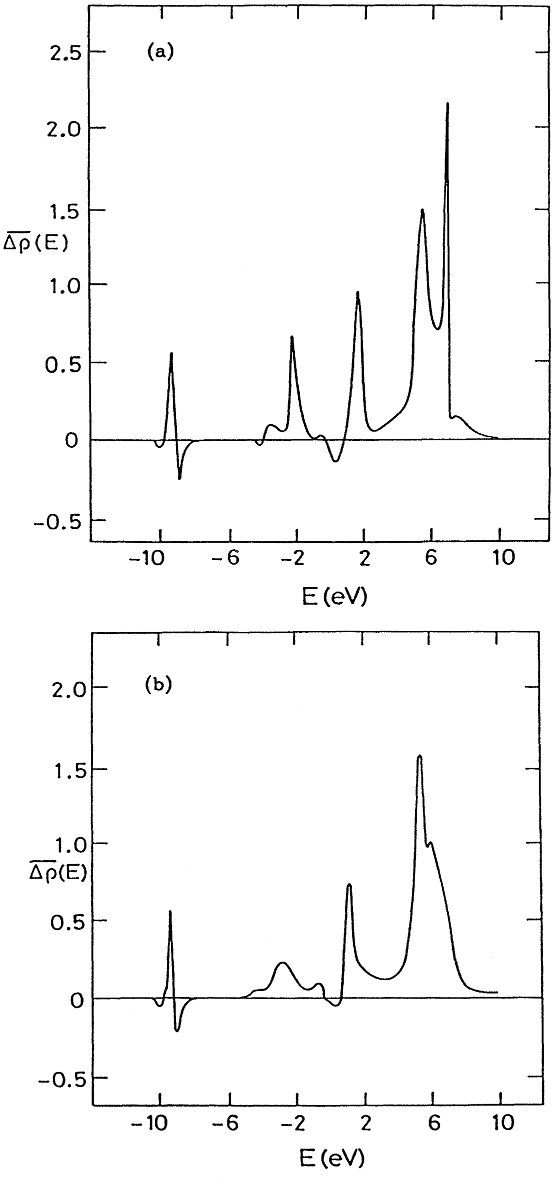

FIG. 3. The changes in the density of states for the adsorption of a Zn atom on a Te-terminated (111) surface of CdTe and HgTe. (a) $\Delta\rho^{AS}(E)$ for CdTe. (b) $\Delta\rho^{AS}(E)$ for HgTe.

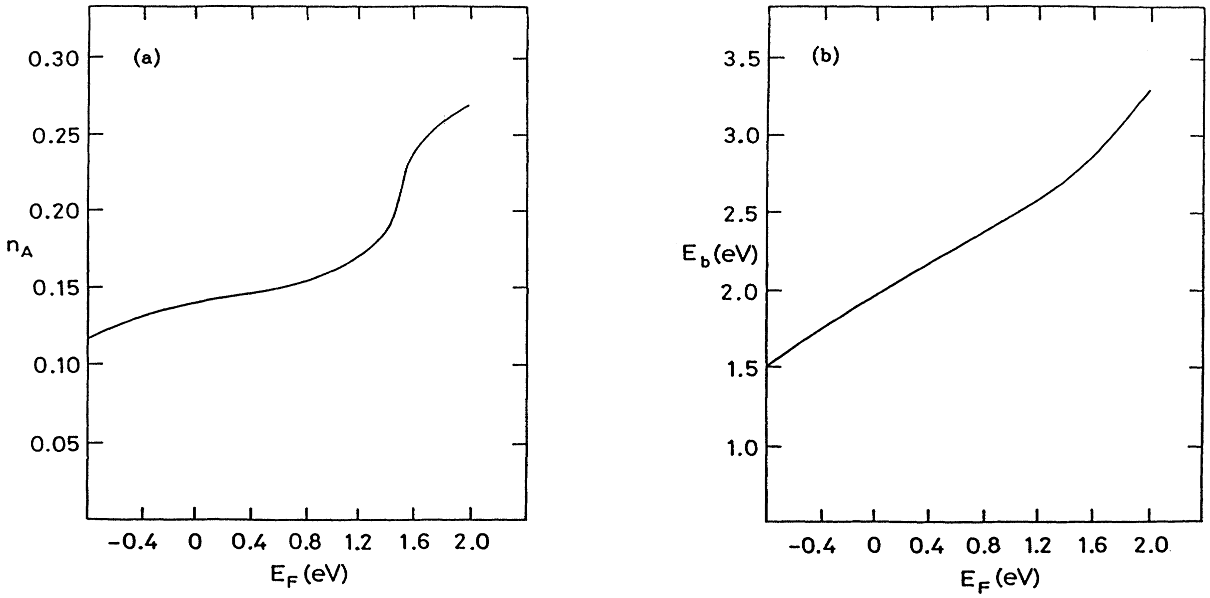

FIG. 4. The occupation number n_A and binding energy E_b for Zn adsorbed on a Te-terminated (111) surface of CdTe. (a) n_A as a function of E_F. (b) E_b as a function of E_F.

IV. CONCLUSIONS

It has been only recently that well-characterized surfaces of II-VI semiconductors have been available for well-defined adsorption experiments. Adsorption of group-II metals on surfaces of II-VI compound semiconductors are of particular interest because such atoms will strongly bond tetrahedrally to anion-terminated surfaces. Knowledge of adsorption properties is essential in the design of passivation layers and for the modification of surface properties such as work functions.

We have developed an approach for calculating adsorption properties which represents a significant improvement over previous work[2] in two key areas. First, we use the empirical tight-binding method to determine realistic bands for the bulk system throughout the Brioullin zone, instead of the Kane model which properly describes only the band edges. Since the creation of the surface involves short-range interactions, details of the band structure in the entire Brioullin zone are important. Second, our adsorbate atom is a specific group-II atom which tetrahedrally binds to the surface with a strength that we can calculate, while Ref. 2 uses a model adatom with a single *s* level. We have used this new method to calculate electronic properties associated with the adsorption of Zn on the (111) Te-terminated surface of CdTe or HgTe.

Our results for the changes in the density of states accompanying the adsorption can be experimentally verified by, for example, angle-resolved uv photoelectron spectroscopy which has been used to characterize CdTe surfaces.[14] Since we are looking only at changes, our results should not be too sensitive to nonlocal details of the uncovered surface. Our predictions for the dependence of the binding energy on the level of doping in the semiconductor can be verified from measurements of heats of adsorption or kinetics of desorption.

The method we have described is quite general and could be extended to describe a number of different experiments. It would be of interest to investigate the adsorption of atoms with valence orbital configurations different from sp^3, and also adatoms which are more ionic in character. Angle-resolved photoemission experiments could provide information on changes in the density of states as a function of layer depth from the surface.

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