Surface-Enhanced Alloy Effects in $Hg_{1-x}Cd_xTe$: (100) Surface States and the Site-Dependent Coherent-Potential Approximation

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The density of states for ideal (100) cation- and anion-terminated surfaces of $Hg_{1-x}Cd_xTe$ ($x=0.5$) have been determined with a site-dependent coherent-potential approximation for the alloy. Alloy effects are greatly enhanced at a cation surface. The cation-surface density of states exhibits HgTe- and CdTe-like surface-state bands with no virtual-crystal—related surface-state features. This bimodal character does not appear in the bulk or anion surface density of states. Similarly, the self-energy at a cation surface site is very different from those in the bulk or near-anion surfaces.

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Alloy effects on the electronic structure of a compound semiconductor alloy depend on how similar the constituents are and how sensitive the states are to fluctuations in local environment. III-V semiconductor alloys, such as $Ga_{1-x}Al_xAs$, are well described by the virtual-crystal approximation (VCA), in which a composition-weighted average cation potential defines the effective cation potential, because the constituent cations are similar. However, recently the VCA was found to be inadequate for the II-VI alloy $Hg_{1-x}Cd_xTe$.[1,2] Relativistic effects present in HgTe, but weak in CdTe,[1-3] lower the Hg 6*s* level so much relative to the Te 5*p* states that HgTe has a zero band gap and an inverted band structure, while CdTe has the normal semiconductor level ordering. Coherent-potential—approximation (CPA) calculations for the alloy density of states of deep valence states[1,2] display atomic-like HgTe and CdTe features not predicted by the VCA but observed by photoemission.[1]

Intuition suggests and model calculations[4-7] confirm that states localized to surfaces or defects are more sensitive to local alloy configurations than well-extended bulk states and require, in an alloy like $Hg_{1-x}Cd_xTe$, a sophisticated alloy approximation. In this Letter we present the first CPA calculation of the surface states of a real semiconductor alloy. All previous realistic calculations[8-15] of surface and defect states in semiconductor alloys have used the VCA. The local densities of states (DOS) at ideal (100) cation- and anion-terminated surfaces and in the bulk of $Hg_{1-x}Cd_xTe$ ($x=0.5$) have been determined. Because the surface breaks the translational symmetry of the lattice, the CPA self-energy is site dependent near a surface. Our results for $Hg_{1-x}Cd_xTe$ show that alloy effects are greatly enhanced at cation surfaces. The use of the generalized site-dependent CPA is absolutely necessary to account for the enhancement. Although the site-dependent CPA was proposed ten years ago[4] and has been used in model calculations,[4-6,16] this is the first use of the site-dependent CPA in a realistic calculation.[17] The model calculations[5,6] have shown that the site-dependent CPA qualitatively reproduces the alloy effects on surface DOS that are predicted by embedded-cluster theories and that it should be reliable for realistic calculations.

Tight-binding (TB) second-nearest-neighbor Hamiltonians developed by Hass,[2] Ehrenreich, and Velický are used to describe HgTe and CdTe. Spin-orbit effects are included by use of a sixteen-state model with cation and anion *s* and *p* states for each spin. Hass, Ehrenreich, and Velický chose the energy levels to be the atomic energies and determined the off-diagonal elements by fitting to experimental energy gaps and pseudopotential calculations. The model is superior to other TB models[13,14,18] for the alloy because the Te energy levels in HgTe and CdTe are the same. In other models the anion energy levels change as much between HgTe and CdTe as the cation levels change even though the anion is the same. We further generalized the Hass-Ehrenreich-Velický model by including couplings previously ignored to obtain more accurate conduction bands and masses.

The Green's-function approach is used to implement the CPA and to determine the bulk and surface DOS. Translational symmetry parallel to the surface exists when the alloy is modeled with the VCA or CPA. Thus the alloy Hamiltonian is diagonal in surface wave vector, $\mathbf{k}_s$, and the realistic calculation can be reduced to a set of one-dimensional chain calculations, one for each $\mathbf{k}_s$ in the surface Brillouin zone. The Green's function for a one-dimensional chain is found by the renormalization-decimation technique.[6] In this approach every other atom on the finite chain is removed (decimation), and the Hamiltonian is renormalized to account for the decimation. The procedure is exact. After N iterations a chain with $2^{N+1}+1$ atoms is simplified to one with three renormalized atoms, one each for the cation and anion surfaces and one for the bulk. This simpler problem is then easy to solve. Typically ten renormalizations are done, corresponding to films with 2049 layers, to eliminate remnants of surface-surface interactions present in thinner films.

In the CPA each cation site is occupied by an effective atom which for the *s* levels is described by self-energies $\Sigma_{\uparrow\uparrow}$ and $\Sigma_{\downarrow\downarrow}$ for each spin together with spin-mixing terms $\Sigma_{\uparrow\downarrow}$ and $\Sigma_{\downarrow\uparrow}$. In principle, similar self-energies describe the cation *p* levels and the coupling between cation *s* and *p* levels. The other parameters that describe the anions and the interatomic hopping are treated in the VCA. The self-energies are determined by the requirement that the effective cation produce the same scattering as the average scattering of Hg and Cd in the effective medium.

The bulk CPA is normally implemented by ignoring the coupling between *s* and *p* levels in the self-energy, the off-diagonal terms that mix spins, and the spin dependence of the diagonal terms. However, the surface breaks translational symmetry, and so there is no reason to neglect spin mixing near the surface. For that reason we use the most general *s* self-energy including $\Sigma_{\uparrow\uparrow}$, $\Sigma_{\downarrow\downarrow}$, $\Sigma_{\uparrow\downarrow}$, and $\Sigma_{\downarrow\uparrow}$. This is the first use of the more general form in a CPA calculation for a semiconductor. As in the bulk CPA, alloy effects from cation *p* levels are small in the surface CPA; thus only the spin-dependent diagonal *p* self-energies are used, and no *s-p* mixing self-energies are included.

The self-energies can be considered to be site dependent for N layers near the surface and to be the bulk self-energies at all other sites. Calculations have been done for $N=0$, 1, and 2. The iterative average-t-matrix approach of Chen[19] is used to find self-consistent self-energies. All of the self-energies are determined simultaneously. No more than five iterations are needed to get accurate solutions. The solutions were obtained at energies with a finite imaginary part ($E_I=0.26$ eV) to speed convergence, and the results were analytically continued to the real axis ($E_I=0.01$ eV) by the procedure of Hass, Velický, and Ehrenreich.[20]

Only results for $x=0.5$ are reported in this Letter because alloy effects should be greatest near this composition. Qualitatively similar results are found for other x values. The results presented are for ideal surfaces. No surface relaxation or reconstruction, surface or bulk ordering, segregation or clustering, or charge transfer not in the TB model have been included because of inadequate available information on $Hg_{1-x}Cd_xTe$ surfaces.

The bulk band structures and surface states of cation-terminated surfaces of HgTe, CdTe, and $Hg_{0.5}Cd_{0.5}Te$ are shown in Fig. 1. The peak of the surface-state feature in the surface DOS is interpreted to be the alloy surface state at a given $\mathbf{k}_s$. This identification is reasonable since the alloy broadening does not smear away the structures. One can see immediately why the VCA is expected to fail for cation surface states of the alloy. Because of the energy difference between Hg and Cd *s* levels, the HgTe surface states are approximately 1 eV lower than the CdTe surface states with little overlap between the bands. Moreover, the states should be sensitive to local alloy effects since they have little dispersion in much of the surface Brillouin zone. While the VCA-alloy surface-state band is approximately the average of the constituent surface-state bands, the surface states found by the general site-dependent CPA retain the character of the individual surface-state bands. The CdTe-like band occurs at lower energy in the alloy than in CdTe because of extra repulsion from the conduction band, which is lower in the alloy. Conversely, the HgTe-like band is at higher energy in the alloy. This bimodal structure was seen in previous model calculations.[6]

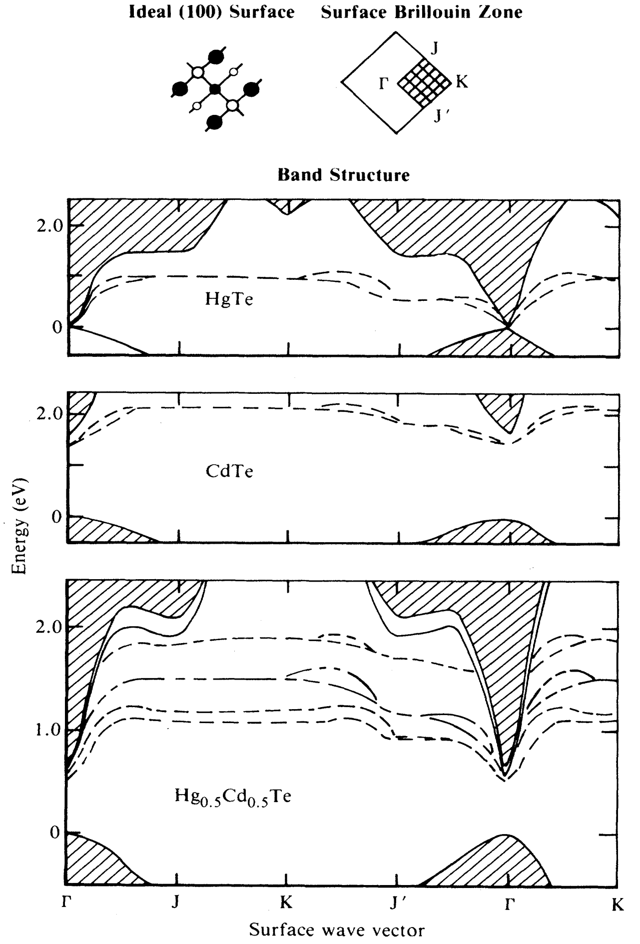

FIG. 1. Bulk and surface-state band structures projected onto the surface Brillouin zone for HgTe, CdTe, and $Hg_{0.5}Cd_{0.5}Te$ with cation-terminated (100) ideal surfaces. The cross-hatched region indicates the bulk bands for HgTe and CdTe and the VCA bulk bands for the alloy. The shifted solid curves are the CPA band edges. The dashed curves are the surface-state bands for HgTe and CdTe and the CPA surface-state bands for the alloy. The long-short dashed curve is the VCA surface-state band. The irreducible sector of the surface Brillouin zone and the first four layers of a (100) surface are also shown. The shaded (open) circles are cations (anions); the largest circles are closest to the surface, and the nearest-neighbor bonds are shown.

The bimodal structure is a direct result of the enhancement of the alloy effects at the cation surface. There is no bimodal character in the bulk bands, and only a small shift exists between the VCA and CPA bulk band edges, except near the zone edges where the bands have less dispersion. The site-dependent results shown in Fig. 1

were obtained with the assumption that only the surface-site self-energies were different from the bulk self-energies. Qualitatively similar results are obtained if the self-energies are different for the first two layers. However, when the bulk self-energies are used for all sites, the bimodal structure disappears. The bulk CPA predicts a single surface state just below the VCA surface state because the bulk self-energy and the VCA energy are so close. Near Γ the VCA, bulk CPA, and general CPA give similar results, with the states shifted to lower energy in the more sophisticated approaches, because the states have large dispersion. However, even at Γ, the enhancement in the DOS above 1.5 eV found by general CPA may be a remnant of the CdTe-like state resonant with the conduction band.

The cation surface-site *s* self-energies shown in Fig. 2 also reflect the surface enhancement of the alloy effects and the bimodal character of the surface-state structure. The real part of the diagonal surface cation *s* self-energy ($\Sigma_{\uparrow\uparrow}$ and $\Sigma_{\downarrow\downarrow}$, where $\Sigma_{\uparrow\uparrow}=\Sigma_{\downarrow\downarrow}$), which is the effective energy of the cation *s* level, has large shifts to Hg-like ($E_s^{\mathrm{Hg}}=-1.32$ eV) and to Cd-like ($E_s^{\mathrm{Cd}}=0.12$ eV) values when the surface states are HgTe- and CdTe-like, respectively. In contrast, the real part of the bulk diagonal self-energy shifts only slightly from the VCA energy except at higher energies (~ 2.0 eV). This slight shift is the signature of the small band-gap narrowing predicted by the CPA.[1,2] The imaginary part of the bulk diagonal *s* self-energy, which gives the alloy broadening, is also small except at high energies. However, the alloy broadening at the cation surface can be several orders of magnitude greater than the broadening in the bulk, especially for states in the region between 1.0 and 2.0 eV, and any VCA-like structure should be broadened away. The *p* self-energies are not shown because the real parts differ from the VCA energies by no more than 0.01 eV, and the imaginary parts are negligible.

The off-diagonal bulk *s* self-energies, $\Sigma_{\uparrow\downarrow}$ and $\Sigma_{\downarrow\uparrow}$, are less than 0.01 eV throughout the energy range shown, so that neglect of them in bulk CPA calculations is reasonable.[1,2] However, the off-diagonal surface cation *s* self-energies are large, comparable in magnitude to the diagonal self-energies, and reflect the bimodal structure in the surface states. While the diagonal self-energies are spin independent and the two bulk spin-mixing self-energies are simply related (one is the negative of the other), the spin-mixing self-energies at a cation surface are not simply related. Not only is the alloy-induced spin mixing enhanced at the surface, but the symmetry is broken as well. Nonetheless, the two spin DOS are still equal.

In contrast to cation surfaces, there is no enhancement of alloy effects at anion surfaces because the states are anion derived. There is no bimodal structure in the alloy anion surface-state band even though the HgTe and CdTe anion surface states do differ slightly. In addition the real part of the diagonal self-energy is closer to the VCA energy for the cation site next to the anion surface than for a bulk site. As in the bulk, the spin-mixing self-energies at the cation site closest to the anion surface are small, although the bulk symmetry between the spin-mixing terms is broken even at the anion surface.

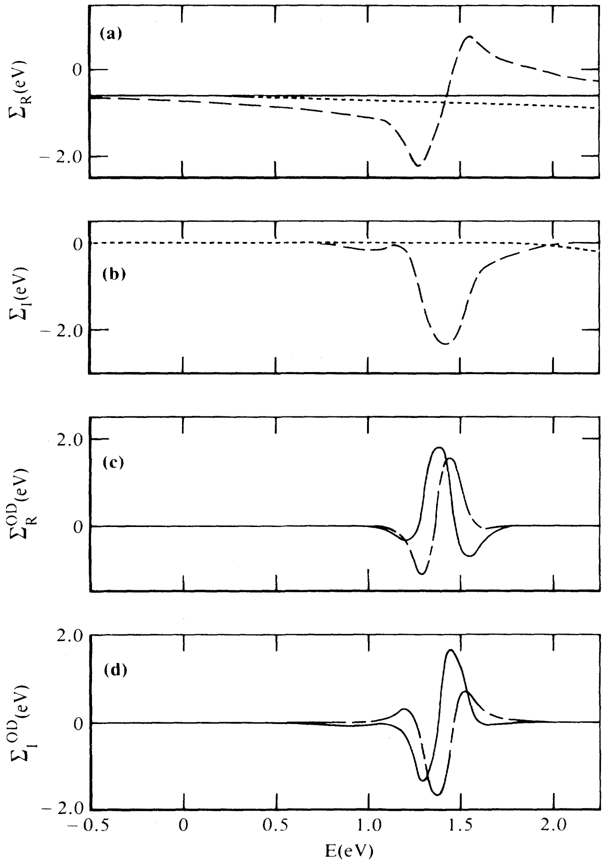

FIG. 2. CPA cation *s*-level self-energy: the (a) real and (b) imaginary parts of the diagonal self-energy (each is the same for both spins), for the VCA bulk (solid curve), CPA bulk (dotted), and CPA cation-surface site (dashed); the (c) real and (d) imaginary parts of the off-diagonal self-energy at a cation-surface site. Both spin-mixing terms are shown.

Several important conclusions can be drawn from the results. Alloy effects are greatly enhanced at a cation surface but not at an anion surface. Great care should be taken in analyzing localized states if they are sensitive to the occupation of the disordered sites. The general site-dependent CPA must be used for surface states because the VCA and bulk CPA give *qualitatively* incorrect results. Finally, the presence of a surface or defect breaks the symmetry, and spin mixing must be properly included as well.

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