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Surface states and surface resonances in InP, InAs, and InSb

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Dispersion curves $E(\bar{k})$ are predicted for both bound and resonant surface electronic states at the relaxed (110) surfaces of InP, InAs, and InSb.

I. INTRODUCTION

The In—group-V compound semiconductors are interesting materials with potentially important device applications. InSb and InAs have small band gaps (about 0.2 and 0.4 eV, respectively, at room temperature), so that InSb, in particular, is a useful infrared detector. InP, on the other hand, has intriguing electronic and optical properties. It is observed to have high mobility (when undergoing n-type doping) and low surface recombination rates[1]; it exhibits resistance to the "rapid" mode of laser degradation,[2,3] and it has a "switchable" Schottky barrier.[4–6]

From a fundamental point of view, the In—group-V semiconductors are of interest because their bulk and surface electronic properties differ from those of the Ga—group-V materials in several respects. For example, the bulk vacancy levels of InP are predicted to lie outside the fundamental band gap,[7] and the surface core excitons[8] are observed[9] and predicted[10] to lie above the conduction-band edges as resonances in InSb and InAs, whereas they lie within the band gap as bound states in all the Ga—group-V semiconductors.[8–10]

Williams and co-workers[11] and other experimental groups are currently investigating the intrinsic surface state bands in InP and the other In—group-V semiconductors. Since it will be of interest to compare theory and experiment, and since the existing theoretical predictions for these materials are rather limited,[12] we have carried out calculations of the dispersion curves for bound and resonant surface states in InP, InAs, and InSb, which we report here. Essential and distinguishing features of the present work are that surface relaxation[13,14] is included and that the energies of the resonant states within the bulk bands are predicted. The (110) surface relaxation is assumed to be the rigid 27.3° rotation of the anions out of the surface plane that is characteristic of all III-V's (Refs. 13 and 14). As shown for GaAs,[15] the rather small changes in bond length that accompany this rotation do not have a substantial effect on the surface state energies. The surface resonances are evaluated as well as the bound states within the gap, because they are fully as important in determining the electronic spectra.[16,17]

II. METHOD OF CALCULATION

The calculations employ the empirical tight-binding sp^3s^* model of the bulk electronic structure[18] and the analytic Green's-function, effective Hamiltonian technique.[19] We have previously calculated the surface state spectra of Ga—group-V,[16] Al—group-V,[20] and Zn—group-VI (Ref. 17) semiconductors using the present approach, and have found that it works remarkably well in each case: (i) The predicted dispersion curves for GaAs and ZnSe are in agreement with the angle-resolved photoemission measurements.[21–24] (ii) All of the direct-gap zinc-blende semiconductors are predicted to have no surface states within the band gap,[15] in agreement with experiment[25–27] and with the previous self-consistent caculations for GaAs.[28–30] (iii) Indirect-gap GaP is predicted to have a surface state band tailing down to an energy below the conduction-band edge,[15] again in agreement with experiment[31,32] and with a subsequent self-consistent calculation.[33] Thus we have every reason to expect the predictions for In—group-V surface states to be comparably reliable.

One of the principal advantages of the sp^3s^* model is that it provides a simple, nearest-neighbor, chemical-bonding picture of surface and defect phenomena in semiconductors, yet (unlike other nearest-neighbor models) is realistic enough to treat conduction-band-related states in indirect-gap semiconductors like GaP.

The calculations are performed as follows: First, the retarded bulk Green's function $G_0^+(E)$ is obtained from the sp^3s^* Hamiltonian and the analytic representation,[19]

$$G_0^+(\vec{x},\vec{x}\,';\bar{k},E) = -2\pi i \Sigma_{k_3} \psi(\vec{x};\bar{k},k_3) \times \psi^\dagger(\vec{x}\,',\bar{k},k_3^*)\,\mathrm{sgn}(x_3-x_3')/v_3(\bar{k},k_3)\ . \tag{1}$$

Here $\vec{x}$ and $\vec{x}\,'$ label lattice points and $\bar{k}$ is the planar wave vector associated with propagation parallel to the surface. The allowed values of the normal wave vector k_3 are those corresponding to the bulk Bloch waves of energy E propagating away from $x_3=x_3'$ (for k_3 real), and the "evanescent waves" decaying away from this plane (for k_3 complex). The wave function is ψ; we define $\mathrm{sgn}(x)=+1(-1)$ for $x>0$ (<0), and v_3 is the group velocity in the direction normal to the surface.

The second step is to calculate the perturbation matrix V, defined by

$$V=H-H_0\ , \tag{2}$$

where H_0 is the (sp^3s^*) Hamiltonian in the perfect crystal and H is the Hamiltonian that results from (i) theoretical cleavage of the crystal along a (110) plane, and (ii) relaxation of the surface atoms with anion atoms rotating outward and In atoms inward. This relaxation is treated by a method similar to that of Chadi.[28]

The third and final step is to locate the energies of the bound states and resonances at each planar wave vector $\bar{k}$. In conventional Green's-function calculations, these energies are found by searching for zeros in the Fredholm determinant (bound states) or its real part (resonances), i.e., from the condition

$$\mathrm{Re}\{[1-G_0^+(E)V]\}=0\ , \tag{3}$$

where $G_0^+(E)$ is the Green's function within the subspace of the perturbation. Our test calculations have shown, however, that it is far more convenient to use the "effective Hamiltonian" technique[19]: Let H_{eff} be defined by

$$E-H_{\mathrm{eff}}(E)=G_0^+(E)^{-1}-V \tag{4}$$

and $E_i(E)$ represent its eigenvalues,

$$H_{\mathrm{eff}}(E)\xi_i(E)=E_i(E)\xi_i(E)\ . \tag{5}$$

The condition for a bound state is

$$E_i(E)=E\ . \tag{6}$$

Since the $E_i(E)$ are typically slowly varying functions of E, Eq. (6) provides a straightforward and numerically efficient procedure for locating such surface bound states.

Within the bulk bands, H_{eff} is no longer Hermitian and its eigenvalues are complex. In this case we define surface resonances by

$$\mathrm{Re}[E_i(E)]=E\ . \tag{7}$$

Details of the method are given elsewhere.[19,34]

III. RESULTS

Our results are shown in Figs. 1–3. The surface states are labeled according to the scheme introduced by Chelikowsky and Cohen for GaAs (Ref. 29): A_i and C_i denote states associated primarily with anion and cation atoms, respectively. A_1, A_2, C_1, and C_2 are mainly s-like, with A_2 and C_2 local-

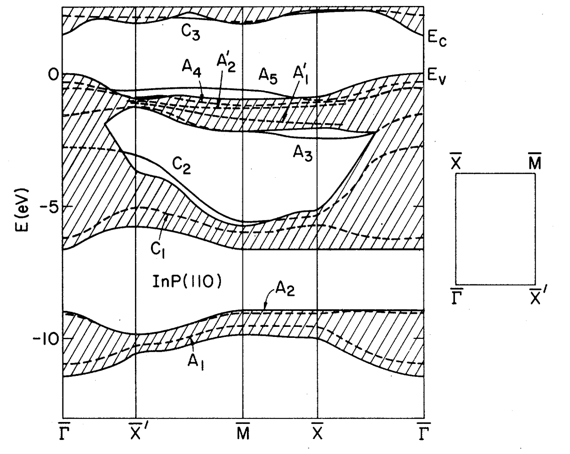

FIG. 1. Dispersion curves for bound states (solid lines) and resonant states (dashed lines) at the relaxed (110) surface of InP. Surface-state energy E is plotted as a function of the planar wave vector $\bar{k}$ for $\bar{k}$ lying along the symmetry lines of the surface Brillouin zone, shown on the right. [$\bar{\Gamma}$ is the origin, $\bar{k}=(0,0)$; $\bar{M}$ is a corner of the surface Brillouin zone, $\bar{k}=(\frac{1}{2},\frac{1}{2})$.] Bulk bands at fixed $\bar{k}$ span the regions indicated by the light diagonal lines. E_v and E_c are, respectively, the valence- and conduction-band edges; the band gap is that measured at low temperature.

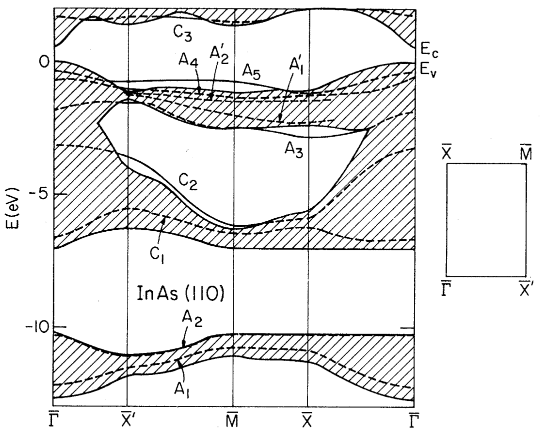

FIG. 2. Dispersion curves for bound and resonant (110) surface states in InAs.

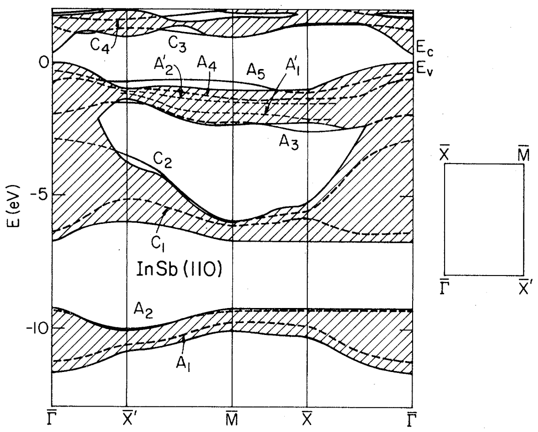

FIG. 3. Dispersion curves for bound and resonant (110) surface states in InSb.

ized largely in the first layer and A_1 and C_1 in the second layer. A_3, A_4, A_5, and C_3 are mainly *p*-like, A_5 and C_3 being the "dangling-bond" bands and A_4 being the "back-bonding" band. $A_{1'}$ and $A_{2'}$ were not reported in Ref. 29; they are largely associated with in-plane *p*-bonding in the first and second layers, as is A_3. We emphasize, however, that the character of each state changes with the planar wave vector and represents an admixture of many orbitals.

Notice that our Green's-function, effective Hamiltonian technique is well suited for the treatment of the surface resonances (dashed lines) within the bulk bands. In the studies of GaAs (Ref. 16) and ZnSe (Ref. 17), we found that these resonances are just as important as the bound surface states. In particular, our calculated resonances were in agreement with experimental features in the surface state spectra of both GaAs (Refs. 21–23) and ZnSe (Ref. 24) that had not been explained by the previous theoretical treatments.

The valence-band-derived surface states are similar to each other, and are also similar to those obtained for the Ga–group-V,[16] Al–group-V,[20] and even Zn–group-VI compounds.[17] This is not surprising, of course, since the bulk valence-band structure is similar for all of these materials having the zinc-blende structure and similar chemical bonding.

The conduction-band-derived surface states, like the bulk conduction bands themselves, show variations from one material to another. In particular, the minimum energy of the lowest unoccupied surface state band is predicted to lie about 0.5 eV above the conduction-band edges E_c in InSb and InP but about 1 eV above E_c in InAs. (This minimum is predicted to lie only slightly above the conduction-band edge in GaAs, and somewhat below E_c in GaP.[15,16]) Of the occupied surface states, only the *s*-like states A_1, A_2, C_1, and C_2 exhibit unambiguous chemical trends; their energies are ordered InP > InSb > InAs. It will be gratifying if the present predictions are borne out by experiments.

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