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Authors
Chadi, D.J.
Cohen, Marvin L.

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D. J. Chadi and Marvin L. Cohen

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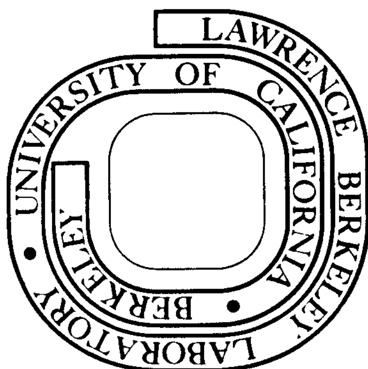

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Tight-Binding Calculations of (111) Surface Densities of States of Ge and GaAs*

D. J. Chadi and Marvin L. Cohen
Department of Physics, University of California, and
Inorganic Materials Research Division,
Lawrence Berkeley Laboratory, Berkeley, California 94720

Abstract

We have used the tight-binding method to calculate the local densities of states of unreconstructed Ge (111) and GaAs (111), $(\overline{111})$ surfaces. In the unrelaxed surface configuration we find two types of states for each surface. The effects of relaxation on Ge surface states are also discussed.

The semiempirical tight-binding (TB) approach to the problem of surface states in Si and Ge is very successful[1] in providing results that are in good agreement with those obtained from more elaborate and accurate calculations.[2] We have used the TB method to study the (111) surface properties of Ge, GaAs and ZnSe. The interaction parameters were obtained by fitting the bulk valence and conduction bands.[3] Very good results, in particular for the valence bands, were obtained by using six parameters for Ge and nine for GaAs and ZnSe.[3] Relaxation was taken into account in a manner similar to that of Pandey and Phillips.[1] The values of the parameters and details of the calculation will be discussed elsewhere.[4]

The local density of states (LDS) of surface atoms and the total density of states for a system consisting of sixteen layers (eight double layers) for Ge in the unrelaxed and relaxed configurations are shown in Figs. 1-2 respectively. The top of the bulk valence band E_v, the Fermi energy E_F and the energy E_s for which the integrated LDS of surface atoms is equal to the total number of surface electrons occur at -0.58, 0, 0.08 eV in Fig. 1 (unrelaxed) and at -1.2, 0.43, -1.6 eV in Fig. 2 (relaxed). The surface states are labelled by S_1, T_1 (Fig. 1) and resonant states giving rise to structure by R_1 and R_2. In Fig. 2 additional surface states S_2 and S_3 are also present. The structure D_1 in both figures corresponds to states having a small dispersion in the Brillouin zone and are not associated with surface states.

The most extensively studied and probably the most interesting surface state is the one labelled S_1 in energy loss spectroscopy.[5] This state is associated with the dangling-bond state. Theoretical calculations usually give the position of the S_1 state to be in the fundamental energy gap region but a number of different experiments[5-12] have given different results for its position. For example photoemission experiments[6,8] suggest that these states lie below[6,7] E_v or very close and slightly above[8] E_v in the case of Si. Optical reflectivity and absorption[12] experiments together with work function and photoelectric threshold measurements[9-11] suggest two sets of surface states: one filled and close to

E_v (or partly overlapping with the valence bands) extending into the gap region, the other empty and also in the gap region. The nature of the surface states near or above E_v are sensitive to the surface potential and atomic arrangement. Surface bands extending into the gap region and also overlapping with bulk valence bands were obtained by Hirabayashi[13] when he used thirteen first and second-nearest neighbor interactions.

We find that the LDS of surface atoms is strongly affected by relaxation. The most important change is a shift of E_s to a lower energy such that it is below E_v and E_F. This shift would cause an excess surface charge density of 0.07 electrons per surface atom (5×10^{13} e/cm^2). This would give rise to band bending and a redistribution of the surface charge, leaving the S_1 peak (in Fig. 2) relatively unoccupied.

The number of states in the S_1 state (assuming it is completely filled) is equivalent to that arising from one electron per surface atom. In the unrelaxed case each surface atom contributes 0.5 electrons to this state, in the relaxed case only 0.15 electrons. The contributions of second and third layer atoms are 0.2, 0.1 electrons respectively (unrelaxed), and nearly the same as in the surface layer for the relaxed configuration. The states labelled by T_1 are associated with back-bonding orbitals and are true (i.e. nonresonant) surface states for wavevectors near K (the

corner of the hexagonal Brillouin zone). Each of the doubly degenerate eigenvalues at K corresponding to T_1 has a weight of 0.4 (0.3) electrons per surface atom in the unrelaxed (relaxed) configurations. The average contribution of surface atoms however is about 0.1 (0.05) electrons in the unrelaxed (relaxed) cases. This state corresponds to the lower transverse back-bonding states obtained by Pandey and Phillips.[1] It has also been obtained in a simpler two parameter[14] model calculation where it can be shown that its occurrence depends on the value of the structure factor describing the atomic positions. The T_1 state appears to be absent for the (110) face of Ge[15] in the unrelaxed surface configuration. The surface states S_2 and S_3 (Fig. 2) result from surface relaxation. The state S_2 arises from a nearly equal mixture of back-bonding orbitals of the first two layers. At the point K of the Brillouin zone the two eigenvalues corresponding to S_2 each has a weight of 0.25 back-bonding orbitals per surface atom. The average contribution is however much smaller and is about 0.04 electrons per surface atom.

The surface states S_3 at the bottom of the valence bands are also associated with back-bonding orbitals. The S_3 type surface states and resonances occur over a range of about 3 eV and each surface atom makes a contribution of nearly 0.3 electrons to this state.

The strong surface resonances at what corresponds to the L_1 peak in bulk Ge are strongly enhanced as a result of relaxation. Surface resonances near the L_1 peak have been observed[8] for a Si 7 × 7 reconstructed surface.

The (111) surface properties of GaAs are also very interesting. This surface is not a cleavage plane, however it has been possible to obtain stable (111) surfaces and photoemission experiments[16] have recently been performed on these surfaces. In Figs. 3a and 3b we show the results of our calculations for the LDS of (111)-Ga and $(\overline{111})$-As surfaces. In addition to these the local density of states of the layer next to the surface and also the total density of states for sixteen atomic layers are shown. We have labelled some of the important structure by $A_0,\ldots,A_4$. The peak A_0 corresponds to the lowest conduction band of GaAs and it is mainly an As antibonding s-state. The peaks A_1 and A_2 correspond to Ga and As dangling-bond surface states respectively. There is a gap of about 0.4 eV between them and each has a width of about 0.6 eV. The Fermi energy E_F is at 0.6 eV midway in the Ga dangling-bond state. Assuming the A_1 peak to be completely filled we find that the Ga-(111) surface atom each contribute 0.32 electrons to this structure. For the A_2 peak we find each As-$(\overline{111})$ surface atom to contribute 0.72 electrons. The back-bonding Ga and As orbitals give rise to the surface states labelled A_3 and A_4. The back-bonding Ga-(111) orbitals each give 0.25 electrons to A_3 and the

corresponding As orbitals give 0.38 electrons to A_4. The surface states A_3 may be difficult to detect because of their complete overlap with bulk states. The structure A_4 should be easier to detect since it has only a relatively small overlap with the bulk band. For a more ionic compound (such as ZnSe) we find the A_2 and A_4 states to be narrower and closer to the bulk bands.

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Resumé

En utilisant l'approximation des liaisons fortes, nous avons calculé les densités d'états locales des surfaces (111) du Germanium, (111) et ($\bar{1},\bar{1},\bar{1}$) de l'Arsennic de Gallium. Dans la configuration où la couche de surface est non déplaceé on trouve deux sortes d'états pour chaque surface. L'effet du déplacement est discuté dans le cas du Germanium.

Figure Captions

Fig. 1. Total density of states (solid line) of Ge for a system of sixteen layers. The surface is taken to be 1×1 and unrelaxed. The local density of surface states (dashed line) is also shown. The integrated densities of states over all states has been set equal for both curves to facilitate comparison between the two. The curves have been smoothed with 0.15 eV wide Gaussian functions to remove noise.

Fig. 2. Total density of states (solid line) of Ge for a system of sixteen layers and for a relaxed surface. The local density of surface states is also shown. See also caption for Fig. 1.

Fig. 3. The total density of states (solid line) of GaAs (unrelaxed 1×1 surface) for a system of sixteen layers (a) and (b). The local density of states (LDS) of the Ga-(111) surface denoted by $[Ga]_1$ and the LDS of the As surface, $[As]_2$ next to $[Ga]_1$ are shown in (a). The corresponding LDS for the As-$(\overline{111})$ surface are shown in (b). See also caption for Fig. 1.

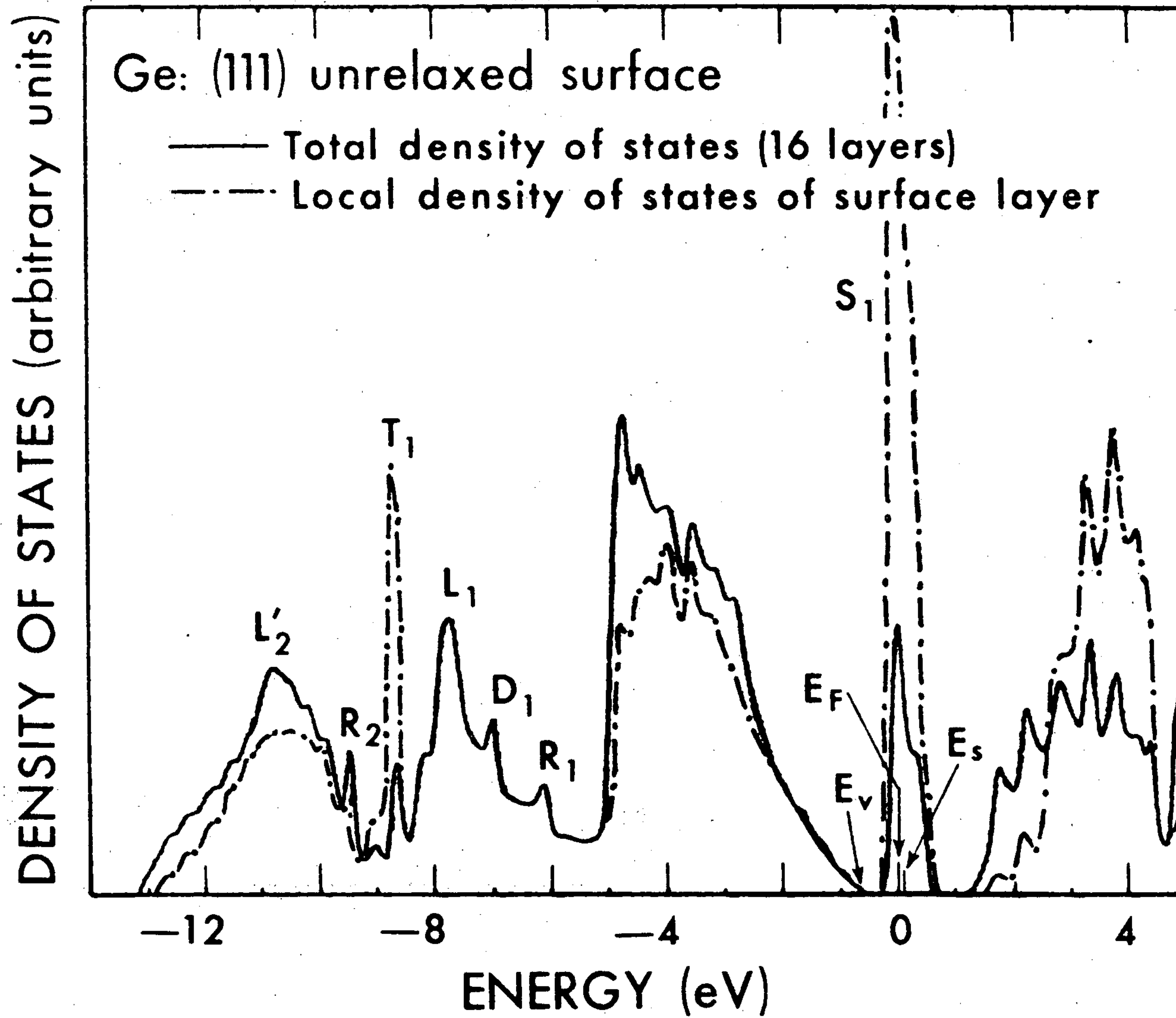

Figure 1

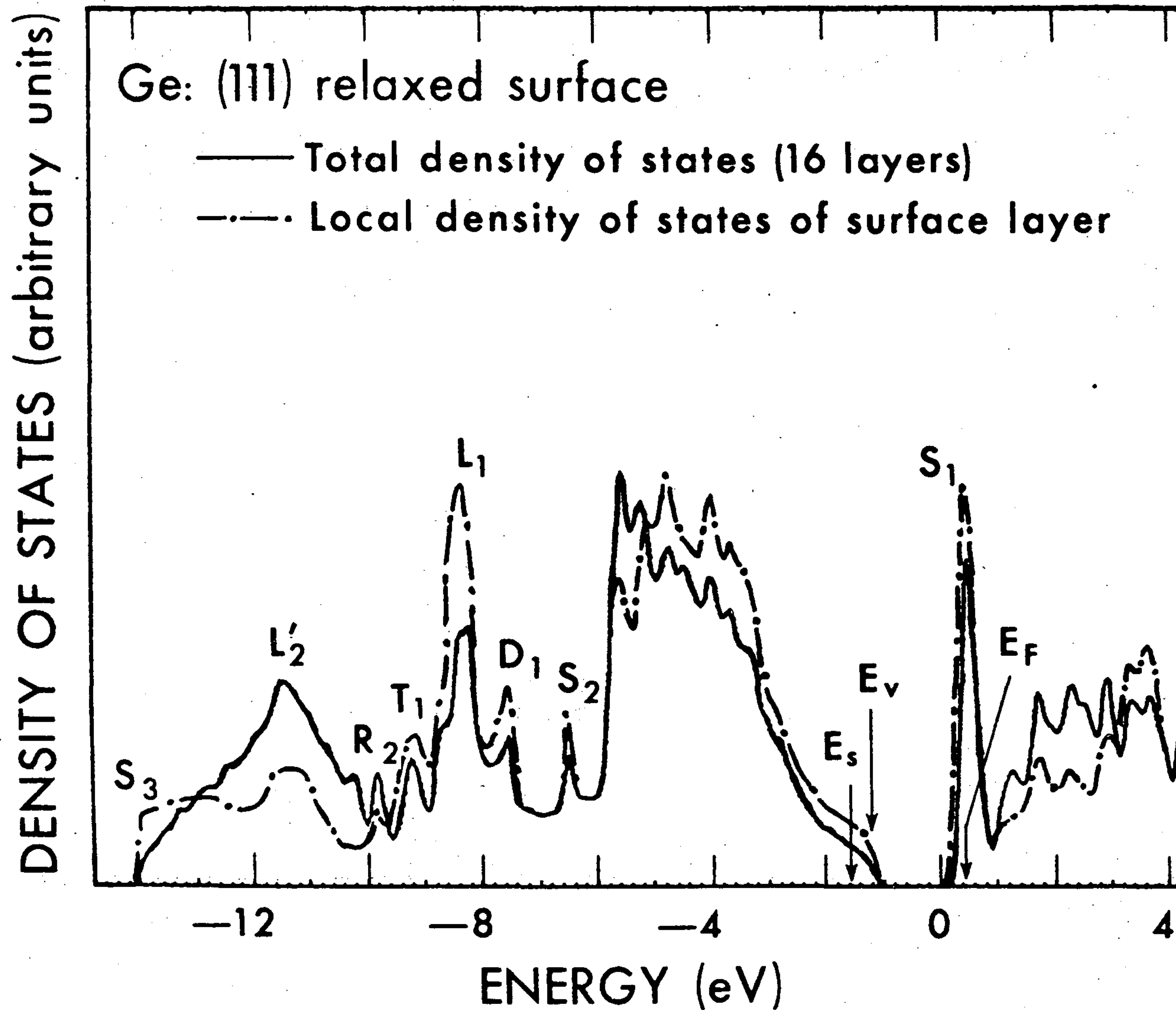

Figure 2

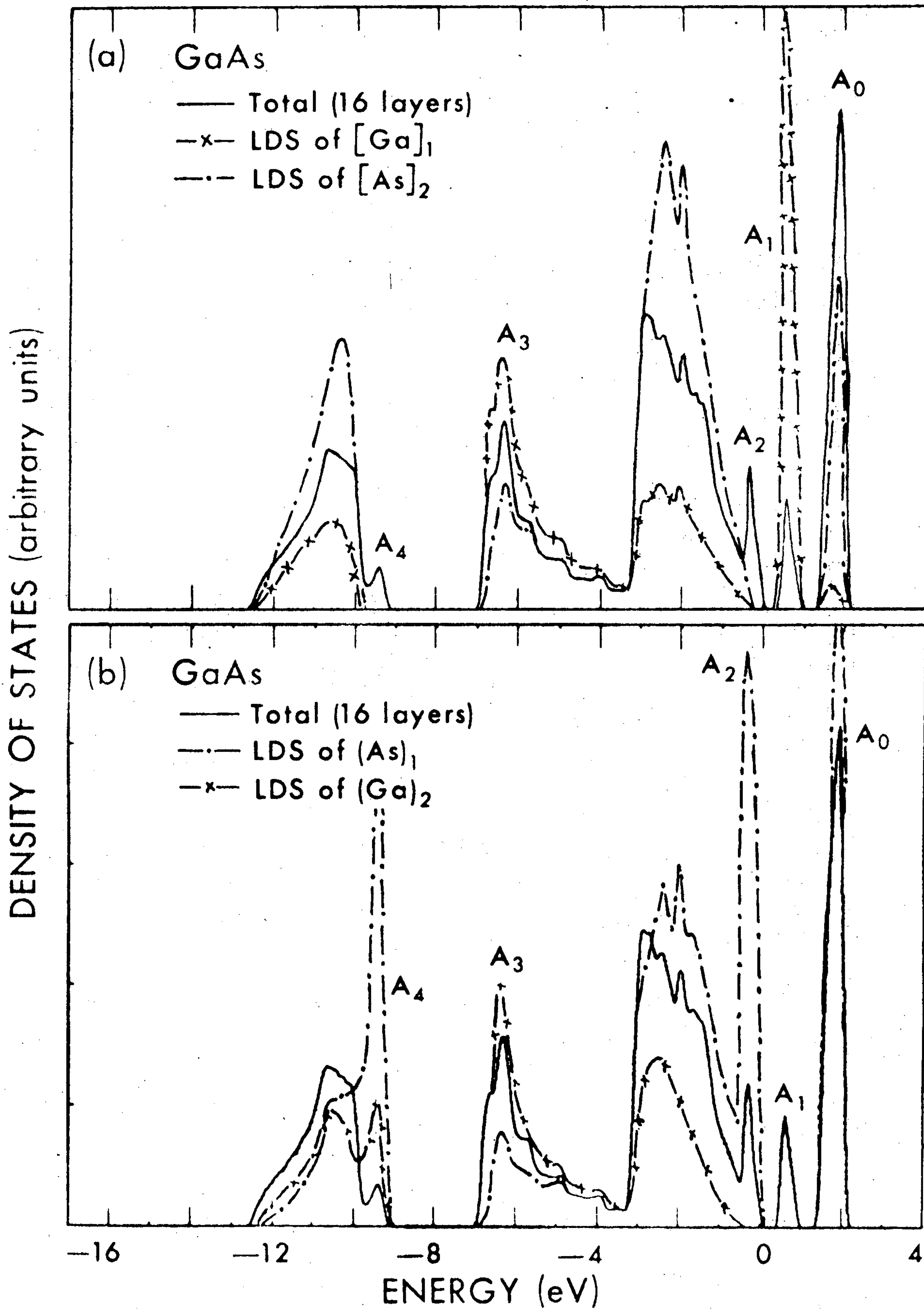

Figure 3

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