Structural and electronic properties of the Al-GaAs(110) interface

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Studies of both the structural and electronic properties of the Al-GaAs(110) interface are presented. It is found that the generally accepted relaxed GaAs(110) surface geometry is energetically unfavorable when the interface with Al is formed. The energy released from the interfacial back relaxation is more than 0.35 eV/(surface atom). Many of the salient features found here are consistent with a previous calculation of the Al-GaAs interface using a jellium model for Al. The presence of a high density of continuum states in the semiconductor energy gap is not sensitive to the interfacial structures, but the details are structure dependent. Estimates of the decay length and density at the Fermi level of the metal-induced gap states for the ideal interface are in good agreement with those from the jellium-model calculation. A new feature, absent in the jellium model, is the formation of Al—As bonds, which substantially reduces the density of states near the top of the valence band.

I. INTRODUCTION

The basic mechanisms involved in the formation of Schottky barriers at the metal and III-V compound semiconductor interface are not well understood. The complexities of semiconductor surfaces and interfaces such as surface relaxation, surface stoichiometry, lattice mismatch and disordering, chemical reaction, interdiffusion, exchange of atoms, presence of defects and metal-induced gap states, etc.,[1-10] make this problem a difficult one. It is known that the Schottky-barrier heights for covalent semiconductors are insensitive to the metal contact.[1] An early model explained the Fermi-level pinning in terms of intrinsic semiconductor surface states.[10] This model is not generally applicable, since, for example, there are no semiconductor surface states in the energy gaps of many III-V and II-VI compounds after surface relaxations.[1,11] Other models have been developed and in particular two[5-9] will be considered here. The idea that local states in the semiconductor energy gap will pin the Fermi level is also an essential feature in these models, even though the two schemes differ. One model is the defect model[5,6] where gap states are provided by the formation of interfacial defects. Some recent work, however, indicates that the density of defects necessary for Fermi level pinning may be much higher than those known to exist at interfaces.[12,13] The other model attributes the pinning of the Fermi level to metal-induced gap states,[7-9] but this approach has been questioned because of the simple treatment of the surface structure, as well as the use of a jellium model for the metal.[1,12,13]

Here, we report new results using GaAs as a prototype semiconductor in contact with Al atoms. We believe that this is the first *ab initio* pseudopotential calculation of the interfacial relaxation of GaAs(110)-Al based on total energy calculations. The calculations show that the relaxed surface is unstable when in contact with thick layers of Al. A high density of continuum states in the gap on the semiconductor side of the interface is found, whether the surface is relaxed or ideal.

II. CALCULATIONS

Al-GaAs(110) is one of the few known interfaces in which the lattice mismatch is small provided that the Al(110) surface is rotated by 90°. Therefore, in our calculations, the GaAs lattice constant is fixed at the bulk value and Al is compressed by about 1.3%. In reality this could be the case for the growth of a thin film of Al on the GaAs(110) surface.

The Al-GaAs(110) interface geometry with an ideal GaAs(110) surface is shown in Fig. 1. The positions of the Al atoms are chosen so that they remain in the fcc structure and the bond length of Al—As is 2.45 Å. This value is taken from the work of Ihm *et al.*[14] who found that for half or one monolayer Al adsorption on the
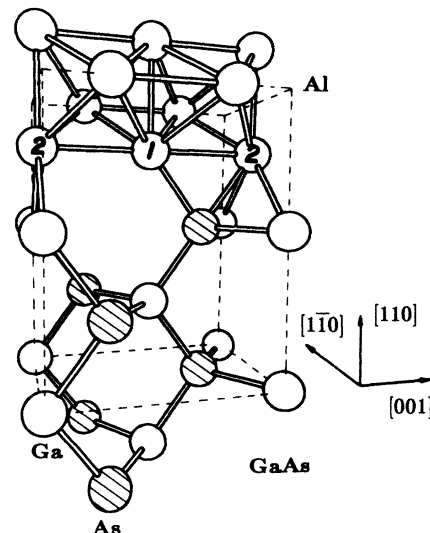

FIG. 1. A perspective view of the ideal Al-GaAs(110) interface. The indices for the crystal directions refer to GaAs. The sticks are drawn to connect each atom with all the neighboring atoms within a distance of 2.83 Å.

GaAs(110) surface this bond length is insensitive to the adsorption site and coverage to within 0.1 Å. In Fig. 1, the Al atoms labeled 1 are in tetrahedral positions with respect to the first layer As atoms while those labeled 2 are at the same distance from the As atoms but not in tetrahedral sites. The distance from Al atom 2 to the first layer of Ga atom, l_{Al-Ga}, is 2.83 Å. Upon relaxation of the GaAs(110) surface, both the Al fcc structure and the bond length of Al—As are kept unchanged; however, l_{Al-Ga} is elongated to 3.36 Å.

Our calculations employ the slab geometry[15] and each supercell contains seven layers of GaAs and five layers of Al atoms. For the relaxed GaAs surface, the surface As atoms are displaced away from their ideal positions by 0.16 Å. The supercell is ~1.5% longer than the one used for the ideal geometry. The relaxed surface structure model used here for GaAs(110) was recently determined by elastic low energy electron diffraction measurements.[3] However, in the present calculation we fix the second layer of GaAs atoms in their ideal positions so that the center region of the GaAs slab is less affected by the surface relaxation. Since the relaxation energy of the second layer GaAs atoms is an order of magnitude smaller than that of the first layer atoms,[16] this approximation should have a small effect on the total energy.

Although supercells with slightly different volumes are used for the two different interface geometries, results for the corresponding clean surface relaxation are consistent with previous calculations.[16] The relaxed free GaAs(110) surface is energetically favorable and is 0.33 eV/(surface atom) lower than the ideal surface. Uncertainties in the differences of the total energies are estimated to be a few percent and the determination of the Fermi levels is within ±0.1 eV.

The calculational scheme has been described in more detail elsewhere.[17−19] We use norm-conserving pseudopotentials,[20] the momentum space formalism[21] for the total energy and the local-density approximation (LDA) with the Ceperley-Alder correlation energy functional.[22] The wave function is expanded in terms of plane waves up to 5 Ry in kinetic energy, corresponding to ~620 plane waves/cell.

III. RESULTS

There are some predictions that the relaxed GaAs(110) surface is unstable for the early stages of Al adsorptions (≤ 1 monolayer).[14,23,24] However, quantitative calculations for the Al-GaAs(110) interface are not available. In our thick layer approach, we find the Al interface with the ideal GaAs(110) surface geometry (geometry I) is 0.35 eV/(surface atom) lower in energy than the Al interface with a relaxed GaAs(110) surface geometry (geometry II). The instability of the latter geometry can be qualitatively understood as being caused by the unfavorable formation of sp^2 hybrids on Ga sites. In the case of the clean cleaved GaAs(110) surface, the formation of sp^2 orbitals pushes the cation surface states up and the anion states down to open an energy gap. As a result, charge is transferred from Ga atoms to As atoms. However, in the

case of the interface, the Al-1 atoms (Al atoms in the 1 positions) form sp^3 hybrids with the surface As atoms and prevent charge transfer from Ga to As atoms. Persistance of GaAs(110) surface relaxation would push electrons into higher energy bands and require extra energy.

In Figs. 2(a) and 2(b) and Figs. 3(a) and 3(b), the charge contour plots in the $(1\bar{1}0)$ plane are shown for geometry I and geometry II, respectively. Figures 2(a) and 3(a) show the Ga-terminated planes and Figs. 2(b) and 3(b), the As-terminated planes. Surface As atoms remain in tetrahedrally bonded environments with Al-1 atoms. A high density peak of the Al—As bond [Figs. 2(b) and 3(b)]
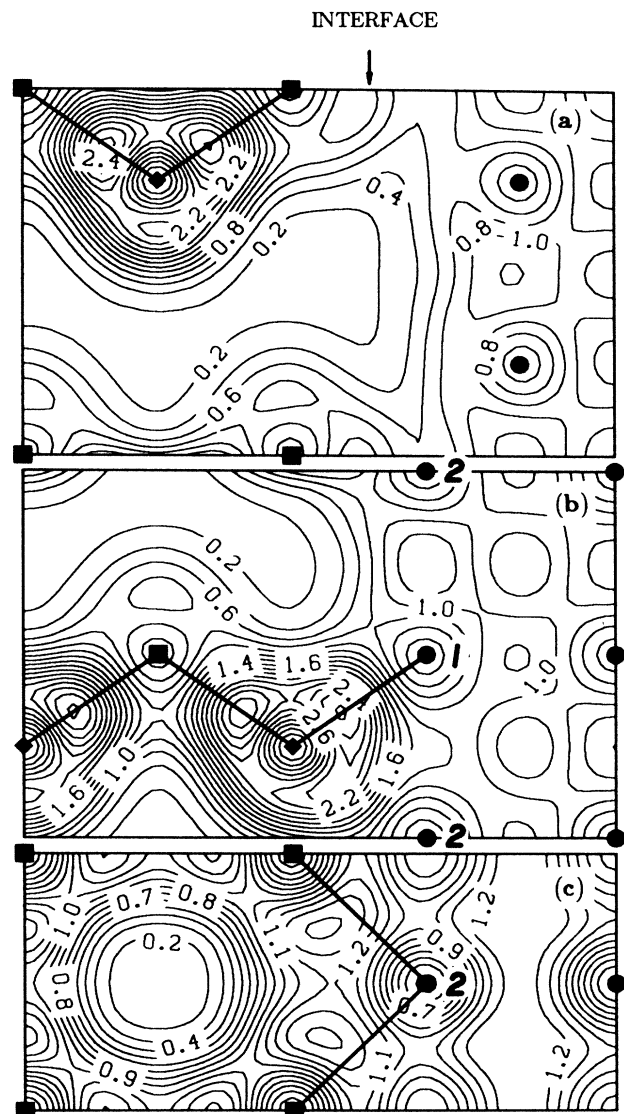

FIG. 2. Solid squares are gallium atoms, solid diamonds are arsenic atoms, and aluminum atoms are denoted by solid circles. Parts (a) and (b) are charge density contour plots in the $(1\bar{1}0)$ plane for the ideal interface. Both Ga- and As-terminated surface planes are shown. Contours are normalized to one electron per supercell and the contour spacing is 0.2 (electrons/supercell). Part (c) is a contour plot in the (001) plane with contour spacing of 0.1 (electrons/supercell).

indicates strong bonding between the Al adlayers and the substrate. Al-2 atoms (Al atoms in the 2 positions) do not form appreciable bonds with the surface As atoms although the distance is the same as the distance from surface As atoms to Al-1 atoms.

The overlap of the wave functions for surface Ga atoms and Al-2 atoms is large in geometry I [Fig. 2(c)] but is much smaller in geometry II (not shown). The distance, $l_{Al—Ga}$ in geometry II is 19% longer than in geometry I. In Fig. 2(c), we plot the charge density for geometry I in the (001) plane which contains both the surface Ga atoms and the Al-2 atoms. Each Ga atom is bonded to two Al atoms. Although such bonding is weak compared to covalent bonding, its bond charge is as strong as the Al—Al metallic bonding. Since Al has a cohesive energy of 3.39 eV/atom[25] with 12 nearest neighbors in the fcc structure, a crude estimate of the binding energy is about 0.6 eV per "bond." Therefore, the Al—Ga bonding energy is expected to be on the order of a few tenths of an electron volt per bond. We tentatively attribute the energy released from the interfacial back relaxation of 0.35 eV/(surface atom) to the formation of the Al—Ga bond, although other mechanisms such as the changes in the interfacial dipole layer characterizing the charge transfer from the metal to the semiconductor may also contribute. It is plausible that the relaxation of the interface will proceed in the opposite direction to the free (110) surface relaxation since the Ga—Al distances tend to be smaller. However, definite conclusions require a calculation of the minimization of interface energy.

The electronic structure of the two interfaces reveals another important aspect of this calculation. Metal-induced gap (MIG) states exist for both geometry I and geometry II. The density of states for the MIG states is defined as

$$D_s(E) = S^{-1} \int_S \int_{-\infty}^0 D_{LDOS}(E,r) dz \, dS, \quad 0 \le E \le E_g \quad (1)$$

where S is the interface area, E_g is the energy gap, and the integral over z is to be evaluated from the bulk region of the semiconductor to the interface. The local density of states $D_{LDOS}(E,r)$ is shown in Fig. 4 for three different regions for the ideal interface geometry. In Figs. 5(a) and 5(b), the density of MIG states as defined by Eq. (1) are shown for both geometries. The density of MIG states is high and is of the same order of magnitude as in the jellium-model calculations.[7] In the ideal interface calculation, the density of MIG states at the Fermi level [$E_F \approx 1.2$ eV in Fig. 5(a)], $D_s(E_F)$ is about 3×10^{14} states/(cm^2 eV) compared to $\sim 4 \times 10^{14}$ states/(cm^2 eV) in the jellium model.[7] For geometry II, $D_s(E_F)[E_F \approx 1.35$ eV in Fig. 5(b)] is higher, because the surface Ga and Al-2
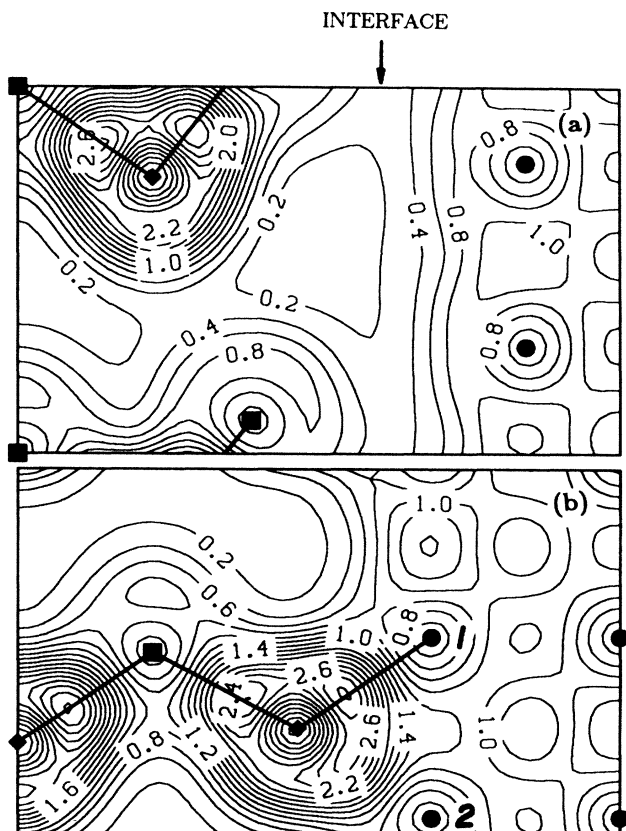
INTERFACE

FIG. 3. Charge density contour plots in the $(1\bar{1}0)$ plane for the interface with a relaxed GaAs surface geometry. Parts (a) and (b) are Ga- and As-terminated surface planes, respectively. The contour spacing is 0.2 (electrons/supercell).
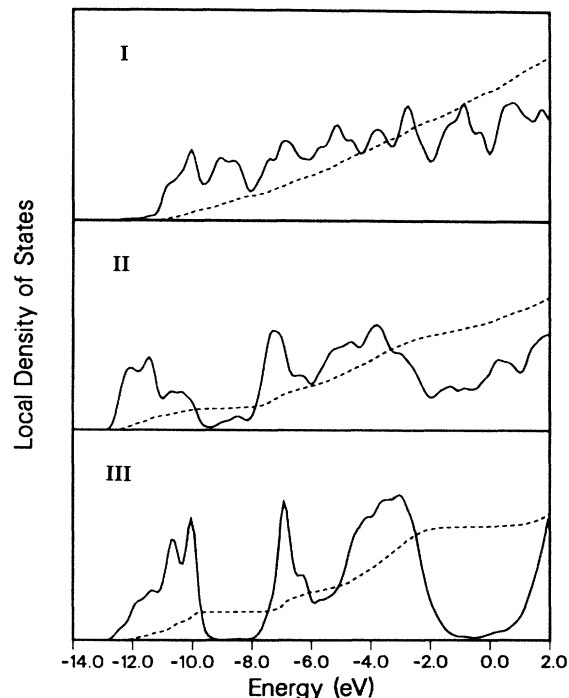

FIG. 4. Local density of states for an ideal interface. It has been normalized to unit volume. The dashed lines are the integrated local density of states. Region I is the Al region; region II is the interfacial region defined as the region from the second layer of GaAs atoms to the first layer of Al atoms; region III is the GaAs bulk region. The densities of states have been Gaussian broadened by 0.2 eV and the zero of energy is fixed at the Fermi level.
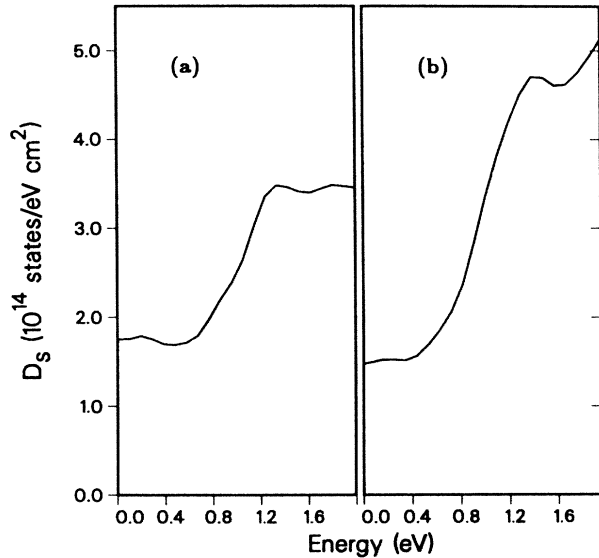
FIG. 5. Density of metal-induced gap states. (a) Geometry I. (b) Geometry II as defined in text.

atoms are less bonded and correspondingly the occupied band energy is higher. The Schottky barrier height for geometry II is 0.15 eV smaller than the value of geometry I. A notable difference between the present results for the ideal interface and the jellium-model calculation is that
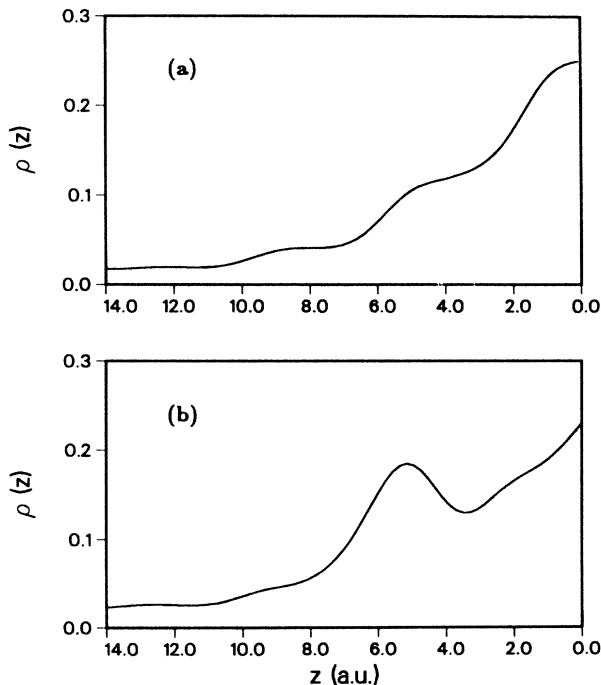

FIG. 6. Charge distributions of the penetrating tails of the MIG states in the GaAs gap averaged parallel to the interface. The interface boundaries are defined as 0.71 Å away from the first layer of Al atoms towards the GaAs surface and are taken as the right boundary of the plots. (The coordinate z is measured from the interface boundary to the semiconductor bulk.) The value of 0.71 Å is half of the distance between two adjacent layers in the bulk Al crystal along the [110] direction. (a) Geometry I. (b) Geometry II.

the density of MIG states in the lower part of the energy gap is smaller by a factor near 2. Compared to the jellium calculation, substantial increases in the surface local density of states at much lower energy near -6.0 eV measured from the top of the valence band are found in Fig. 4. The charge density for states in the energy range from the top of the valence band to the Fermi level shows characteristics of Ga—Al bonding across the interface. This indicates that the band energy of the As dangling bond in the jellium-model calculation has been replaced by the band energy of the As—Al bond at much lower energies in the present calculation. A similar result was found for the early stage of Al adsorption on the GaAs(110) clean surface.[26] Even though the jellium model does not provide a complete treatment for interfacial bonding, the reduced density of MIG states is still high enough to pin the Fermi level.

The decay of the charge density of the MIG states is illustrated in Fig. 6. For geometry I, the decay is similar to that obtained in the jellium model and the decay length is 2.96 Å compared to the jellium value of 2.8 Å. For the interface with a relaxed GaAs surface, a peak appears at about 2.75 Å from the interface boundary [Fig. 6(b)]. The extent of the wave functions for some MIG states near the interface boundary in the ideal geometry has moved further into the interior regions of GaAs in this relaxed geometry. Hence, the effective length entered in calculating interface dipoles should be longer.

IV. DISCUSSION

Our results for the electronic structure of the interface confirm the presence of a high density of MIG states with decay lengths similar to the jellium-model results. Hence the interfacial dipole moment can vary over a large range. Any model dealing with interfacial dipoles has to take into account the evolution of the surface states into MIG states which are not simple WKB tunneling states.

Although our calculation still employs simplified structural models for the metal-semiconductor interface, it is clear that the presence of MIG states is not very sensitive to the interfacial geometry. For the two models we studied, the local density of states anywhere inside the energy gap is high enough to pin the Fermi level. In contrast, the density of surface states in the gap is quite different for the two clean surfaces. The fact that the Fermi level evolves at small metal coverages can be understood as a result of both a slow buildup of MIG states and interfacial back relaxation, i.e., the removal of the GaAs(110) surface relaxation. When the process stops, the Fermi level is pinned. The energy released in this process is high, 0.7 eV/(surface cell), and is possibly important for the formation of Ga vacancies at the surface which is related to the replacement of Ga atoms by Al atoms.[4] We have confined our discussions to the interfacial regions of a few Å. It is possible that defects introduced by the growth of the interface extend over a larger scale of the order of hundreds of Å. The density required for Fermi level pinning in this case is low compared to that of the MIG states. Such a long-range pinning mechanism does not provide information about the interfacial region on a mi-

croscopic level and it cannot explain why the Fermi level is pinned at low metal coverages.

Because our calculation uses the local density approximation, it does not give a clearly defined result for the calculated Schottky barrier height even though the calculated value is close to the experimental value of 0.8 eV. The calculated energy gap in this study is 1.96 eV which is larger than the converged LDA result.[27] It is, however, interesting that the Fermi levels lie on the shoulder of the density of MIG states which can be considered as the onset of conduction-band-derived MIG states. Tersoff's model[28] predicts that layer-by-layer charge neutrality of the system will require the Fermi level to lie close to a canonical energy level where MIG states change from valence-band-derived states to conduction-band-derived states. He argued that charge neutrality is maintained by

the metallic screening of the MIG states. However, the electronic screening mechanism is not perfect as pointed out earlier.[29] A change in the semiconductor surface structure can cause appreciable change of the barrier height. On the other hand, charge neutrality also governs interfacial relaxation and tends to reduce the interfacial dipole as is seen in the present calculation. The interfacial dipole for geometry I is smaller than its value in geometry II with a net change of 0.03 in atomic units.

ACKNOWLEDGMENTS

[1]L. J. Brillson, Surf. Sci. Rep. 2, 123 (1982).

[2]S. Y. Tong, A. R. Lubinsky, B. J. Mrstik, and M. A. van Hove, Phys. Rev. B 17, 3303 (1978).

[3]C. B. Duke, S. L. Richardson, A. Paton, and A. Kahn, Surf. Sci. 127, L135 (1983); C. Mailhiot, C. B. Duke, and D. J. Chadi, Surf. Sci. 149, 366 (1985).

[4]R. Z. Bachrach and R. S. Bauer, J. Vac. Sci. Tech. 16, 1149 (1979); R. Z. Bachrach, R. S. Bauer, J. C. McMenamin, and A. Bianconi, in Proceedings of the 14th International Conference on the Physics of Semiconductors, Edinburgh, 1978, edited by B. L. H. Wilson, Inst. Phys. Conf. Ser. 43 (Institute of Physics, Bristol, 1979), p. 1073.

[5]W. E. Spicer, I. Lindau, P. R. Skeath, C. Y. Su, and P. Chye, Phys. Rev. Lett. 44, 420 (1980).

[6]W. E. Spicer, P. Chye, P. R. Skeath, C. Y. Su, and I. Lindau, J. Vac. Sci. Tech. 16, 1422 (1979).

[7]S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 15, 2154 (1977).

[8]S. G. Louie and M. L. Cohen, Phys. Rev. B 13, 2461 (1976).

[9]V. Heine, Phys. Rev. A 138, 1689 (1965).

[10]J. Bardeen, Phys. Rev. 71, 717 (1947).

[11]A. Huijser, J. van Laar, and T. L. van Rooy, Surf. Sci. 62, 472 (1977).

[12]W. A. Harrison, J. Vac. Sci. Tech. B 3, 1231 (1985).

[13]C. B. Duke and C. Mailhiot, J. Vac. Sci. Tech. B 3, 1170 (1985).

[14]J. Ihm and J. D. Joannopoulos, Phys. Rev. Lett. 47, 679

(1981); Phys. Rev. B 26, 4429 (1982); J. Vac. Sci. Tech. 21, 340 (1982).

[15]M. Schluter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B 12, 4200 (1975).

[16]D. J. Chadi, Phys. Rev. B 19, 2074 (1979).

[17]W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[18]M. L. Cohen, Phys. Scr. T1, 5 (1982).

[19]M. T. Yin and M. L. Cohen, Phys. Rev. B 25, 7403 (1982).

[20]D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. 43, 1494 (1979).

[21]J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C 12, 4409 (1979).

[22]J. P. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).

[23]E. J. Mele and J. D. Joannopoulos, Phys. Rev. Lett. 42, 1094 (1979); J. Vac. Sci. Tech. 16, 1154 (1979).

[24]D. J. Chadi and R. Z. Bachrach, J. Vac. Sci. Tech. 16, 1159 (1979).

[25]C. Kittel, Introduction To Solid State Physics, 5th ed. (Wiley, New York, 1976), p. 74.

[26]J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Solid State Commun. 20, 641 (1976).

[27]S. Froyen and M. L. Cohen, Phys. Rev. B 28, 3258 (1983); G. B. Bachelet and N. E. Christensen, ibid. 31, 879 (1985).

[28]J. Tersoff, Phys. Rev. Lett. 52, 465 (1984).

[29]S. B. Zhang, M. L. Cohen, and S. G. Louie, Phys. Rev. B 32, 3955 (1985).