Electronic structure of Si and Ge (111) surfaces and the Si-Ge (111) interface

Bal K. Agrawal

Department of Physics, University of Allahabad, Allahabad 211002, India
(Received 6 February 1984; revised manuscript received 19 June 1984)

The electronic density of states for Si and Ge (111) surfaces and of the Si-Ge(111) interface has been calculated using a cluster Bethe-lattice method. The calculated surface and interface states are in reasonable agreement with the available photoemission data. No interface state is seen in the mutual energy gap of Si and Ge, a fact predicted earlier by the author for the Ge-GaAs and Ge-ZnSe interfaces.

I. INTRODUCTION

Intensive experimental and theoretical investigations of solid surfaces and interfaces are being made mainly for three reasons: first, a desire to understand the mechanism that drives the heterogeneous catalysis by noble-metal and transition-metal surfaces; second, device fabrication and characterization, e.g., heterojunctions, Schottky diodes, metal-oxide semiconductor field-effect transistors (MOS-FETs), etc., involve the various types of semiconductor surfaces and interfaces; and, finally, the desire to answer fundamental questions associated with the possible effects of the breakdown of periodicity normal to the surface on the elementary excitations of the systems.

A spurt in experimental investigations has been due to the advancement made in the ultrahigh vacuum technology, achieving vacuum of less than 10^{-10} torr, and the development of molecular-beam-epitaxy techniques, allowing the fabrication of well characterized heterostructures.

The Si(111) surface is the most extensively studied semiconductor surface. The dangling bonds of an ideal (111) surface makes it chemically very reactive and, thus, sensitive to geometry changes, allowing enhanced binding between surface atoms and eventually leading to surface reconstruction. The clean Si(111) surface, thus, occurs in three different structural forms: a metastable (2×1) cleavage face which undergoes a phase transition into a (7×7) stable structure upon annealing up to $\sim 350\,°C$, and a simple (1×1) phase obtained at high temperature by quenching from $\sim 800\,°C$. The (7×7) phase is also preceded by an apparent (1×1) structure in a small temperature region.

The electronic surface states of the Si(2×1), Si(7×7), and Si(111) structures have been studied by experimental techniques like ultraviolet photoelectron (UPS) and electron energy-loss (EELS) spectroscopy. The author is not aware of similar experimental measurements on the (1×1) structure. A number of calculations have, however, been performed on the Si(111) surface. We refer to the review articles of Schluter,[1] Cohen,[2] and Pollmann[3] for earlier work and to Pandey,[4] Chadi,[5] and Northrup, Ihm, and Cohen[6] for the most recent theoretical work.

On the other hand, the study of the Si(111)-Ge interface has not drawn much attention. However, the study of the Si-Ge interface is interesting for several reasons.

First, there is evidence that the Si-Ge interface is abrupt and the interdiffusion of atomic species through the interface is absent. This is not true for other well studied lattice-matched interfaces like Ge-GaAs and Ge-ZnSe,

where interdiffusion of atomic species has been reported. The simple theory of enthalpy mixing of binary solid solutions of covalent semiconductors predicts segregation of atomic species for a large lattice mismatch (the difference between the lattice constants of the atomic species) between the end components of the solid solution.[7,8] For Si-Ge heterojunctions there occurs a mismatch of 4% in the lattice constants of Si and Ge crystals, driving the interface to become abrupt. However, this gain in simplification of theory by the occurrence of an abrupt interface is lost in the complexities arising from the presence of lattice distortion at the interface. It is energetically favorable in the region of the interface to develop misfit dislocations. The germanium crystal exhibits plastic properties and can, thus, sustain a large number of dislocations which, in turn, will lead to the unsaturated chemical bonds called dangling bonds. The minimum number of such dangling bonds would be approximately $6 \times 10^{13}/cm^2$ for a layer of Ge containing about 8×10^{14} atoms/cm^2 on a Si crystal surface.[8] The number is significant and will produce electronic states both in the gap and valence-band region of the bulk accessible to experimental measurements.

Second, electron energy-loss[9] and photoemission measurements[10] have recently been performed on germanium-covered Si(111) surfaces. A tight-binding calculation of the surface energy bands for a slab consisting of 16 layers of Si substrate and an ordered monolayer of Ge at each surface was also made by these authors.[9,10] No account of lattice mismatch was taken in this calculation. Apart from the interface states lying deep in the bulk region, their results predicted the ocurrence of interface states lying deep in the fundamental gap region of bulk Si. In fact, as shown in the present Brief Report, interface states in the gap would not originate from the Si-Ge interface, but instead may appear as the surface states of the Ge-monolayer considered in the slab calculation.

In an earlier paper[11] (hereafter referred to as I) the present author made a detailed study of the electronic structure of a number of (111) semiconductor surfaces, Schottky diodes, and the heterojunctions of Ge, GaAs, and ZnSe using a cluster Bethe-lattice method (CBLM). The results were in qualitative and semiquantitative agreement with pseudopotential[12,13] and other tight-binding calculations. No true interface states, i.e., localized states lying in the mutual gap of Ge-GaAs and Ge-ZnSe interfaces, were observed in agreement with the available experimental data for the (100) Ge-GeAs interface of Esaki, Howard, and Heer.[14] The electronic structure for the ideal (111)-(1×1) surface of diamond has also been reported[15] by the present author.

The dangling-bond band lying in the wide gap has been seen to be extremely flat.

In the present paper, the CBLM method is further applied to the Si(111)(1×1) surface and to the Si(111)(1×1)-Ge interface. The calculated surface/interface states are in agreement with the available photoemission data for (2×1) structures. The present results for the (111) structure should be equally applicable to the (100) and (110) surfaces/interfaces.

II. THEORY

A Bethe lattice is an infinite aperiodic open structure devoid of any closed rings of interatomic bonds. The symmetries of this lattice can easily be exploited to find exact solutions for inhomogeneous systems. One can extend the CBLM to extended perturbations like surfaces or interfaces. Here, for each medium one generates a two-dimensional system with one side kept free for surface study or connected to a similar two-dimensional counterpart of the second medium for interface study.

A nearest-neighbor tight-binding Hamiltonian has been used to generate the electron energies for silicon and germanium, bulk, surface, or interface. The calculation considers the interaction integrals for the s and p orbitals as parameters which have been used earlier[16] (hereafter referred to as II) in a similar cluster Bethe-lattice calculation for the Ge_xSi_{1-x} alloys. The parameters are determined after matching the electron energies at the symmetry points of the crystalline phases.

One defines a Green's function $\underline{G}$ for a system by

$$\underline{G} = (E\underline{I} - \underline{H})^{-1} , \tag{1}$$

where E is the excitation energy, $\underline{I}$ the unit matrix, and $\underline{H}$ the Hamiltonian for the system which can be split as $\underline{H} = \underline{H}^0 + \underline{V}$ with $\underline{H}^0$ denoting the intra-atomic orbital interactions and $\underline{V}$ the interatomic interactions.

The Dyson equation can then be written as

$$(E\underline{I} - \underline{H}^0)\underline{G} = I + \underline{V}G . \tag{2}$$

The equations for the various matrix elements of the Green's function can be written down as an infinite set. However, they can be reduced to a finite set by exploiting the symmetries of the Bethe lattice which give rise to a relation between the Green's function for two more distant neighbors as well as that for the two nearer neighbors.

The local density of states at atom i is then determined by

$$N_i(E) = -\frac{1}{\pi} \mathrm{Im}\,\mathrm{Tr}\langle i|\underline{G}|i\rangle . \tag{3}$$

For details, we refer to papers I and II.

III. CALCULATION AND RESULTS

A. Si(111) and Ge(111) surfaces

The calculation for the ideal Si(111) surface having a (1×1) structure has been performed using the tight-binding parameters for the interaction integrals given by Chadi and Cohen[17] and fixing the sp hybrid-bond energy at zero. The local density of states (LDOS) at a bulk atom, a surface atom, and at an atom lying in a layer below the surface are shown in Fig. 1.
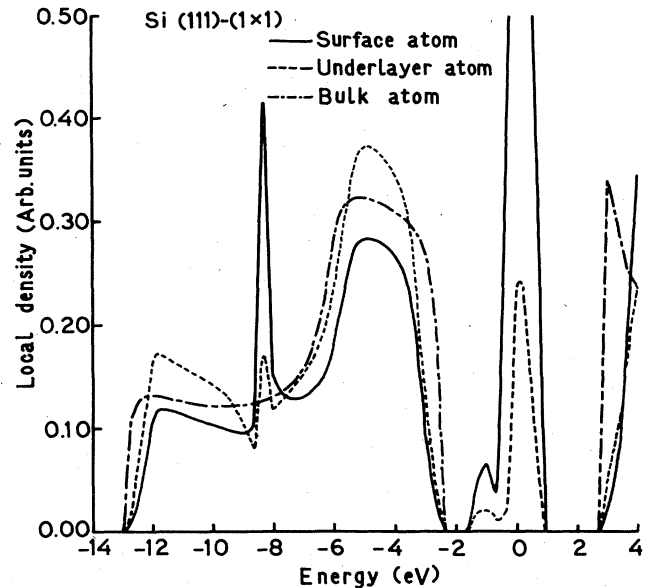

FIG. 1. Calculated electronic LDOS at the various layers for Si(111)-(1×1) surface (a) (——) surface Si atom, (b) (---) next layer Si, and (c) (− · − ·) bulk Si atom.

For a Bethe lattice, the energy bands are usually somewhat contracted because of the absence of long-range interactions. A perusal of Fig. 1 reveals that one obtains enhancement in the LDOS both at the surface atom as well as at the next layer atom. The localized states extend up to the next atomic layer of the surface. A broad band of dangling-bond states appears in the middle of the gap. Incidentally, the dispersive nature of the gap states has been seen in the recent measurements of Uhrberg, Hansson, Nicholls, and Flodstrom.[18] Himpsel, Hermann, and Eastman[19] have found evidence for the occurrence of two surface dangling-bond bands, the upper one dispersive and the lower one dispersionless, which have been accounted for recently[5,6] by assuming a π-bonded chain model.

Furthermore, there appears to be a strong s-like backbond surface band at ∼ −8.2 eV both on the surface and on the next atoms. Also, an enhancement in the states is observed at the next Si atom in two regions around −5 eV (mainly p-like) and around −11.5 eV (s-like). As no experimental data are available for the high-temperature (1×1) structure, we make a tentative comparison of the calculated peaks with the photoemission spectra available for the (2×1) structure by Hansson et al.[20] The calculated peaks near 0.0, −5.0, −8.2, and −11.5 eV are in agreement with the observed peaks, namely, those labeled A, C, D, and H by Hansson, respectively.

For the Ge(111)-(1×1) surface, a similar structure in the electron density of states is observed and one observes here also four peaks at positions which are quite near to those obtained for the Si(111) surface mentioned above. Nicholls, Hansson, Uhrberg, and Flodstrom[21] have observed a highly dispersive dangling-bond surface state in their angle-resolved photoemission measurement for the cleaved Ge(111)-(2×1) surface.

Our results are in qualitative and semiquantitative agreement with the theoretical results of a self-consistent pseudo-

potential calculation of a relaxed Si(111)-(1×1) surface by Schluter, Chelikowsky, Louie, and Cohen.[22]

B. Si-Ge(111) interface

We employ the values of the tight-binding parameters for pure Ge and Si given by Chadi and Cohen.[17] However, the relative positions of the s- and p-orbital energies for Ge and Si have been readjusted to match the tops of the valence bands for bulk Ge and Si near zero, i.e., at ~ 0.3 eV similar to our earlier calculation[16] for Ge_xSi_{1-x} alloys. For the Si-Ge bonds, the interatomic interaction parameters have been taken as the average values of the corresponding parameters for the constituent Ge and Si atoms. The values used have been quoted in paper II. These parameters for Si are different from those used for the Si(111) surface in Sec. III A. No account of the distortion due to lattice mismatch was taken in the calculation. We discuss its effects in Sec. IV.

The computed electron density of states for atoms lying in the interface layer, next layer, and the bulk layer for Ge and Si are shown in Figs. 2(a) and 2(b), respectively. The enhanced density at the interface on both the Ge and Si atoms over the corresponding bulk atoms is depicted in Fig. 3.

As is the case with all the Bethe-lattice calculations, the generated electron density bands are somewhat contracted and the reproduced gaps are larger. As is clear from Fig. 2, there are positive and negative changes in the density throughout the whole valence bands. There are no interface states in the mutual gap of the bulk Si and Ge.

The changes are more evident in Fig. 3, where the excess density over the bulk has been plotted for both the Si and
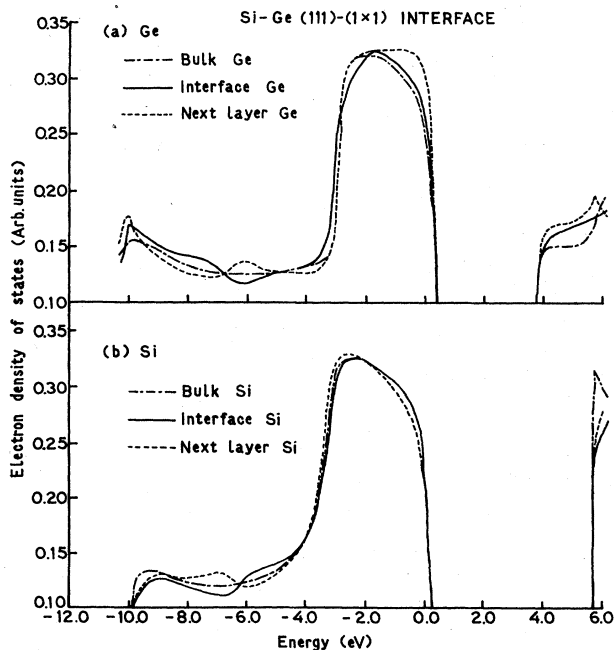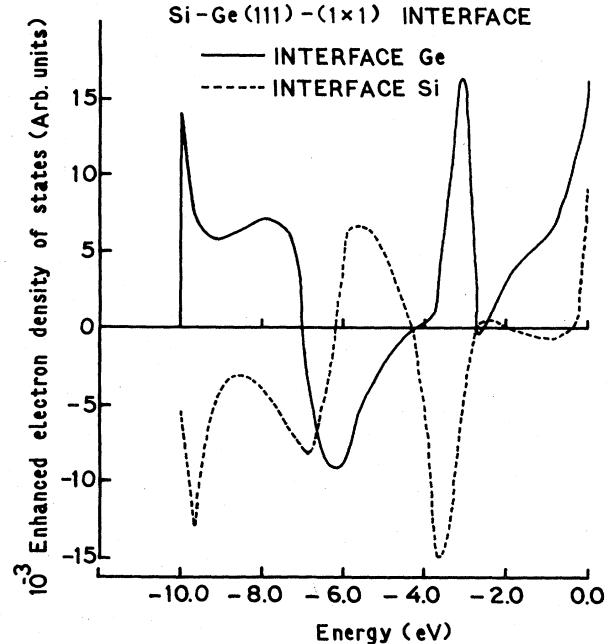

FIG. 3. Enhanced LDOS over the corresponding bulk ones on interface Ge and Si layers. (a) (———) interface Ge, (b) (— — —) interface Si.

Ge layers of the interface. At the Ge interface layer, enhanced density is obtained in the region 0 to -2 eV, near -3 eV and in the region -7 to -10 eV. A peak in the increased density at the Si atom is seen around -5.5 eV.

Comparing the present results with recent photoemission measurements,[10] two peaks have been detected near -5 and -8 eV which are in good agreement with the presently calculated peaks at -5.5 and -8 eV, respectively. Also, a higher interface density of states has been detected in the measured data in the -9 to -10 eV region at higher coverages of Ge on Si(111). However, the extra interface states calculated near the top of the valence band in the present calculations and in the tight-binding calculation of Nannarone et al.[9] have not appeared in the measured data. A careful measurement is needed to clarify the present situation.

IV. DISCUSSION AND CONCLUSIONS

In the above calculation we have lined up the tops of the valence band (E_v) of bulk Si and Ge. However, if one lines up the midpoints of the energy gaps of the two substances, E_v for Ge would be about 0.2 eV higher than of Si. Perfetti et al.[10] have observed the Ge valence-band edge lying above the Si valence-band edge and measured a valence-band discontinuity of 0.15–0.21 eV for the Si-Ge heterojunction. In that case, similar to the cases of Ge-GaAs and Ge-ZnSe interfaces studied earlier,[11] the Si interface layer would pick up some extra states in the said region of 0.2 eV. The present results would remain unaffected and the mutual gap would not contain any interface state.

There is sufficient evidence[23] that the effects of the quantitative disorder (the variations in the bond lengths, bond angles, and dihedral angles) on the electron energy spec-

FIG. 2. Calculated LDOS at the various interface layers for Si-Ge(111) interface. (a) (i) (———) interface Ge atom, (ii) (— — —) underneath Ge layer atom, and (iii) (— · — ·) bulk Ge layer atom; (b) (i) (———) interface Si atom, (ii) (— — —) underneath Si layer atom, and (iii) (— · — ·) bulk Si layer atom.

trum of bulk covalent semiconductors are not very important. Some extra localized states appear at both the top of the valence band and at the bottom of the conduction band. The shifts in the electron energies in the fundamental gap due to bond-length variation is about ± 0.02 eV, and due to band angle variation is about ± 0.2 eV. The topological disorder, i.e., the presence of even or odd numbered rings of atoms incur some changes in the lower region of the valence band.

In the present study we have not considered any lattice mismatch between Ge and Si lattices. In fact, there exists a mismatch of about 4% in the lattice parameters of bulk Ge and Si. The present results would not change much due to this mismatch. The distortion due to the lattice mismatch can be accounted for in the present theory by varying the interaction matrix elements and the directions of the bonds near the interface. This will cause a small redistribution in the electronic density of states. However, no interface states in the mutual gap would result. The gap states lying deep into the mutual gap would arise only from the dangling

bonds present at the interface. As discussed earlier in the introduction, the lattice mismatch in Ge-Si heterojunction region would give a significant number, $6 \times 10^{13}/\text{cm}^2$, of dangling bonds. They will produce gap states in the mutual gap region.

In conclusion, a simple cluster Bethe-lattice calculation which has earlier been seen to give valuable new information about the physics of the amorphous semiconductors in pure and alloyed forms, is able to predict the new features associated with the surfaces and interfaces in a qualitative and semiquantitative manner. All the main features seen in the photoemission data for the Si(111) surface and the Si-Ge(111) interface can well be understood by CBLM.

ACKNOWLEDGMENTS

[1]M. Schluter, in *Festkörperprobleme: Advances in Solid State Physics,* edited by J. Treusch (Vieweg, Braunschweig, 1977), Vol. XVII, p. 155.

[2]M. L. Cohen, in *Advances in Electronics and Electron Physics,* edited by L. Marton and C. Marton (Academic, New York, 1980), p. 1.

[3]J. Pollmann, in *Festkörperprobleme: Advances in Solid State Physics,* edited by J. Treusch (Vieweg, Braunschweig, 1980), Vol. XX, p. 117.

[4]K. C. Pandey, Phys. Rev. Lett. **47**, 1913 (1981); **49**, 233 (1982).

[5]D. J. Chadi, Phys. Rev. B **26**, 4762 (1982).

[6]J. E. Northrup, J. Ihm, and M. L. Cohen, Phys. Rev. Lett. **47**, 1910 (1981); J. E. Northrup and M. L. Cohen, J. Vac. Sci. Technol. **21**, 333 (1982).

[7]M. B. Panish and M. Ilegems, in *Progress in Solid State Chemistry, Vol. 7,* edited by H. Reiss *et al.* (Pergamon, New York, 1972).

[8]V. T. Bublik, S. S. Gorelik, A. A. Zaitsev, and A. Y. Polyakov, Phys. Status Solidi B **66**, 427 (1974).

[9]S. Nannarone, F. Patella, P. Perfetti, C. Quaresima, A. Savoia, C. M. Bertoni, C. Calandra, and F. Manghi, Solid State Commun. **34**, 409 (1980).

[10]P. Perfetti, N. G. Stoffel, A. D. Katnani, G. Margaritondo, C. Quaresima, F. Pattela, A. Savoia, C. M. Bertoni, C. Calandra, and F. Manghi, Phys. Rev. B **24**, 6174 (1981).

[11]Bal K. Agrawal, Phys. Rev. B **23**, 2995 (1981).

[12]W. E. Pickett, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. **39**,

109 (1977); Phys. Rev. B **17**, 815 (1978).

[13]W. E. Pickett and M. L. Cohen, Phys. Rev. B **18**, 939 (1978).

[14]L. Esaki, W. E. Howard, and J. Heer, Surf. Sci. **2**, 127 (1964).

[15]Bal K. Agrawal, Solid State Commun. **35**, 971 (1980).

[16]Bal K. Agrawal, Phys. Rev. B **22**, 6294 (1980).

[17]D. J. Chadi and M. L. Cohen, Phys. Status Solidi B **68**, 405 (1975).

[18]R. I. G. Uhrberg, G. V. Hansson, J. M. Nicholls, and S. A. Flodstrom, Phys. Rev. Lett. **48**, 1032 (1982).

[19]F. J. Himpsel, P. Hermann, and D. E. Eastman, Phys. Rev. B **24**, 2003 (1981).

[20]G. V. Hansson, R. Z. Bachrach, R. S. Bauer, D. J. Chadi, and W. Gopel, in *Proceedings of the Conference on the Physics of Semiconductor Surfaces and Interfaces,* Paris, 1979 [Surf. Sci. **99**, 13 (1980)].

[21]J. M. Nicholls, G. V. Hansson, R. I. G. Uhrberg, and S. A. Flodstrom, Phys. Rev. B **27**, 2594 (1983).

[22]M. Schluter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. B **12**, 4200 (1975); S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, J. Vac. Sci. Technol. **13**, 790 (1976).

[23]J. D. Joannopoulos, Phys. Rev. B **16**, 2764 (1977); F. Yonezawa and M. H. Cohen, in *Fundamental Physics of Amorphous Semiconductors,* edited by F. Yonezawa (Springer-Verlag, Berlin, 1981), p. 119.