Localized electron states in a random stacking of silicon bilayers

W. Y. Ching and Ming-Zhu Huang*
Department of Physics, University of Missouri—Kansas City, Kansas City, Missouri 64110

D. L. Huber
Department of Physics, University of Wisconsin, Madison, Wisconsin 53706
(Received 17 November 1983)

The electronic states of randomly stacked Si bilayers are studied using a first-principles linear-combination-of-atomic-orbitals method. States at the conduction-band edge are found to be all highly localized. At the top of the valence band there is a boundary separating strongly localized states from those which are quasidelocalized. A possible experimental test is suggested.

It is well known that all electron states in a random one-dimensional system are localized.[1] Recently, there has been an upsurge of theoretical work to explore the analytic properties of such a system.[2] In these studies a model Hamiltonian is usually assumed which is sufficiently simple to allow detailed analytic studies. In this Rapid Communication we discuss electron states in a realistic model of a one-dimensional disordered system. In the crystallographic (111) direction Si atoms can stack in $AA'BB'CC'$-$AA'BB'CC'\ldots$ sequence as in the diamond (D) structure or they can stack in a $AA'BB'AA'BB'\ldots$ sequence as in the hexagonal (H) wurtzite structure. If the stacking sequence of the bilayers is completely random in AA', BB', and CC', we have randomly stacked bilayers of Si atoms.[3] This system, which has perfect two-dimensional hexagonal symmetry in the x-y plane but has no periodicity in the (111) z direction, represents a realistic one-dimensional model with diagonal and off-diagonal disorder. Since the local environments of a Si atom in D-Si and H-Si structure are the same up to the second nearest neighbor (NN), the random stacking sequence in the z direction introduces disorder the effect of which is beyond the second NN interaction. Additional disorder may be introduced in a controlled manner without destroying the symmetry in the x-y plane by demanding that the Si–Si bond length (BL) between the atoms within the bilayer have a Gaussian distribution from bilayer to bilayer of relative width δ about the normal Si–Si BL. By varying δ, we can study numerically a one-dimensional system with different degrees of disorder.

We have used a first-principles orthogonalized linear-combination-of-atomic-orbitals (OLCAO) method[4] to calculate the electron states of a supercell of 200 randomly stacked Si layers (100 double layers) with periodic boundary conditions imposed in the z direction. The crystal potential and the basis functions used in the calculation reproduce the band structure of D-Si (Ref. 5) with an indirect band gap of about 1.17 eV which agrees with the low-temperature experimental estimate.[6] The density of states is comparable to the best *ab initio* self-consistent calculations for bulk Si.[7] Since all the multicenter integrals occurring in the Hamiltonian matrix are calculated up to the 6th NN,[4] the effect of the disorder due to interactions beyond the second NN is fully reflected in both the Hamiltonian and the overlap matrix elements and hence in the subsequent wave functions. After orthogonalization to the core[4] the effective basis per Si atom consists of only $3s$, $3px$, $3py$, and $3pz$ orbitals, and for a 200-layer system, the diagonalization of an 800×800 matrix equation yields the energy eigenstates and wave functions. Let $\psi_n(\vec{k},r)$ be a normalized wave function of the nth band, where $\vec{k}$ is a point in the two-dimensional Brillioun zone (BZ). By means of a Mulliken population analysis,[8] each state n can be decomposed into charges ρ_α^n associated with each atomic site

$$\sum_{\alpha=1}^{200}\rho_\alpha^n=\int|\psi_n(\vec{k},r)|^2d^3r=1\ .$$

For a homopolar system considered here, this scheme gives a very good description of the charge distribution of each electron state over various atomic sites. A localization index or inverse participation ratio for the state n is then defined as

$$L_n=\sum_{1}^{200}(\rho_\alpha^n)^2\ .$$

For a finite system of N layers considered here, L_n varies between $O(1/N)$ for a completely delocalized state to 1 for a completely localized one. The reciprocal of L_n is identified as a measure of the number of layers in which the state n has significant amplitude. As noted above, all of the states in an infinite random chain are localized. In a finite one-dimensional system, however, one cannot distinguish between localized states whose spatial extent exceeds the dimension of the system and states of infinite extent as, in both cases, $L_n\sim1/N$. Nevertheless, it is useful to compare the localization indices of the 200-layer random array with those obtained from a 200-layer model of D-Si. The results of the latter calculation[9] are shown in Fig. 1(a). We use the largest L_n in the D-Si supercell calculation, 0.008, as a benchmark in the analysis of the random system. States with $L_n\gg0.008$ are localized well within 200 layers, while those with $L_n\sim0.008$ are regarded as quasidelocalized in the sense that they extend over regions at least as large as 200 layers.

In Fig. 1(b), the L_n for the 200 randomly stacked Si layers with $\delta=0$ are shown. It is clear that highly localized states near band edges are superimposed on quasidelocalized states throughout the valence band (VB) and the conduction band (CB) regions. It is surprising to note that near the CB edge all the states are highly localized. Near the top of the VB a boundary between localized and quasidelocalized states of VB appears about 0.05 eV below the band

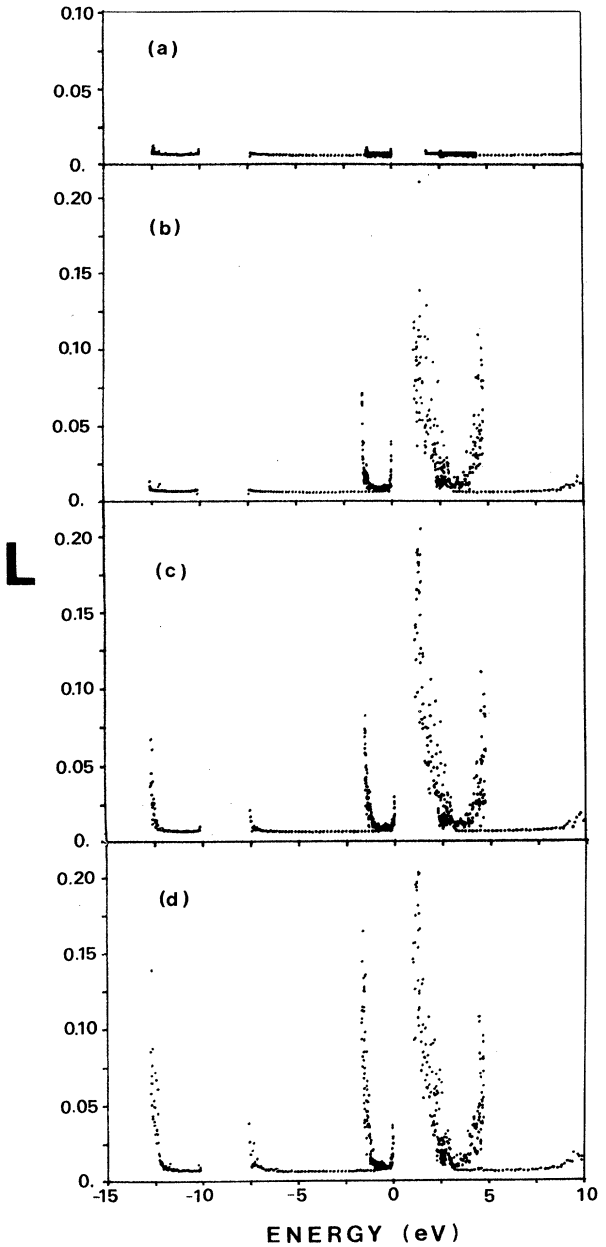

FIG. 1. L_n for electron states at $k=0$: (a) Perfect D-Si. 100 random stacking Si bilayers with (b) $\delta=0$, (c) $\delta=0.012$, (d) $\delta=0.024$. The zero of the energy is set at the top of the VB.

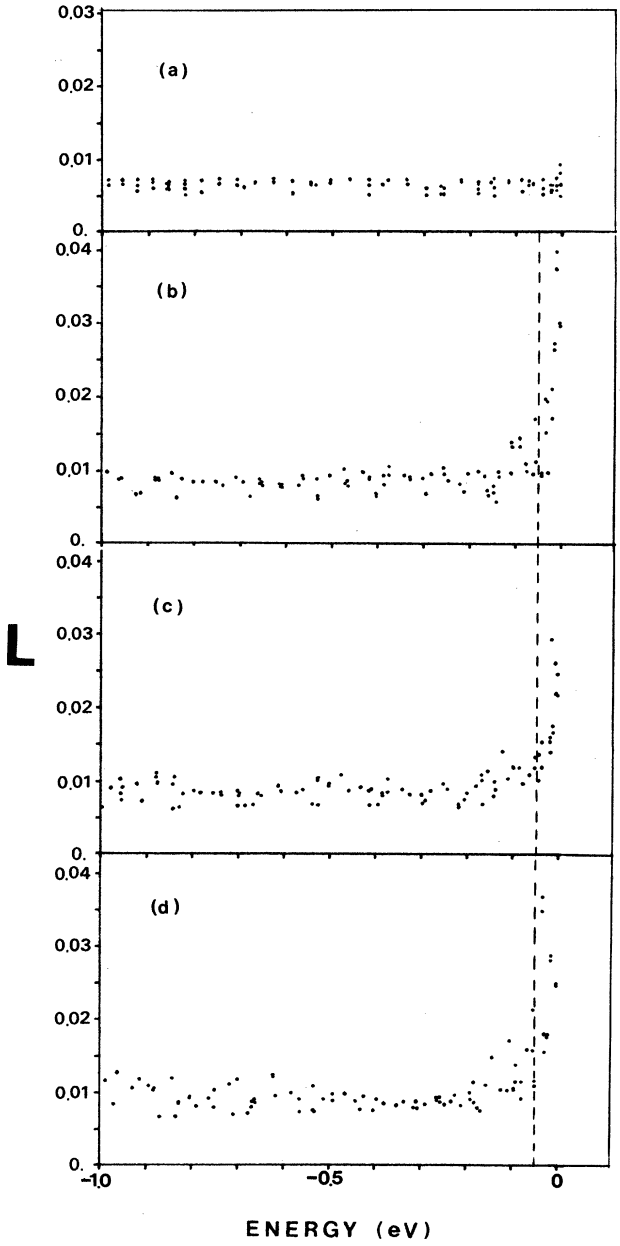

FIG. 2. Enlarged version of Fig. 1 for states near the VB edge. The dotted line is the estimated location of the boundary between highly localized and quasidelocalized states.

edge, as shown in Fig. 2 with enlarged scale. In Figs. 1(c) to 1(d) and 2(c) to 2(d), respectively, we display the results of a calculation in which additonal disorder is introduced in the Si-Si BL between the bilayer atoms. These correspond to $\delta=0.012$ and $\delta=0.024$ for (c) and (d), respectively. From Figs. 1(a)—1(d) it is reasonable to say that the additional BL disorder affects only the states near the low-energy side of the occupied band edges, leading to an increase in L_n, while the states at the top of the VB are little affected so that the boundary remains about -0.05 eV. The results shown in Figs. 1 and 2 correspond to the case $\vec{k}=0$, the center of the two-dimensional Brillouin zone (BZ). We are able to study only one additional $\vec{k}$ point, $2\pi/a$ (1,0), away from zone center at which the matrix equation is real, and calculations indicate that for this point states are in general more localized than the $\vec{k}=0$ case.

It is instructive to investigate the spatial extent in the z direction of each of the localized states in various regions of Fig. 1. Of particular importance are the states at the top of the VB. In Figs. 3(a)–3(d) we display the ρ_n^α for the top VB state against the z coordinates of the αth atom in the stacking layer. Using the full width at half maximum of $\rho_n^\alpha(r)$ as an estimate of the spatial extent of the localized state, we determine the localization region to be about 7 BL (16.5 Å) for randomly stacked Si bilayers as indicated in Fig. 3(b). When additional BL disorder is introduced in the

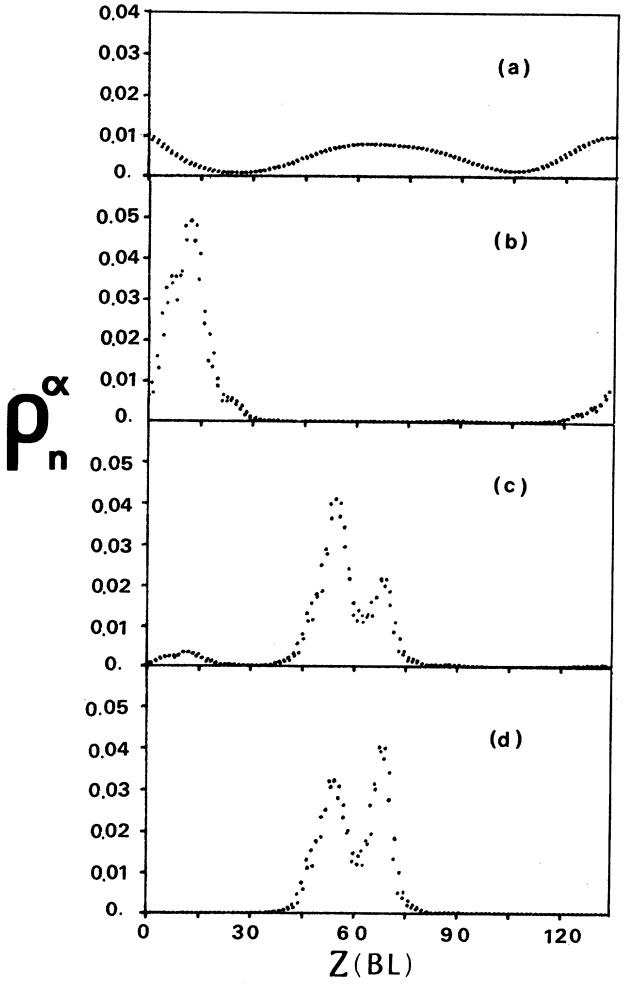

FIG. 3. Plot of ρ_n^α against Z_α for the top VB state. The range of Z_α equals the thickness of 100 Si bilayers (133 Si–Si BL or 313 Å). (a) Perfect D-Si. (b), (c), (d) Random stacking Si bilayers with $\delta = 0$, 0.012, and 0.024, respectively.

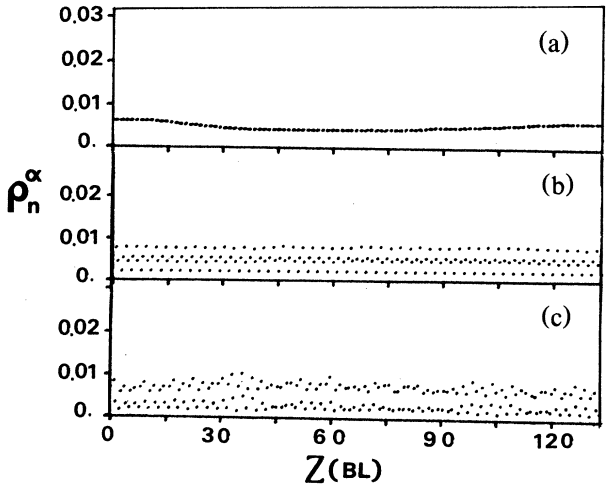

FIG. 4. ρ_n^α for three quasidelocalized states for random stacking Si bilayers with $\delta = 0$ at (a) −10.2 eV, (b) −4.3 eV, (c) 7.0 eV.

bilayer, the states at the top of the VB region tend to localize on two centers separated by about 15 BL, each with a localization region of 7–10 BL. These are shown in Figs. 3(c) and 3(d) for the two cases of $\delta = 0.012$ and $\delta = 0.024$, respectively. In each case, we find the spatial extent of the two top states appears to be almost identical reflecting the bilayer structure. In Fig. 4 we display the ρ_n^α for three quasidelocalized states of Fig. 1(b) near −10.2, −4.3, and 7.0 eV. The amplitudes of the wave functions are seen to extend over the entire region. Since the existence of intrinsic and extrinsic types of stacking faults[10] as well as the H-Si phase[11] in D-Si has been established, it may be possible to prepare samples of randomly stacked bilayers of Si or similar materials (e.g., SiC) using modern experimental facilities for submicrostructures. For the case of low carrier concentration, electron-electron interaction within the CB is expected to be small and one-electron theory for CB states is probably adequate. Direct experimental measurement of the CB electron mobility in the (111) direction should indicate that electron conduction is severely impeded by the localized nature of the states. This opens the possibility of confining the movement of injected electrons to the x-y plane.

In conclusion, we have presented the first realistic calculation of the wave functions of an array of randomly stacked Si bilayers. Our major observations are as follows: (i) All states near the CB edge are strongly localized. (ii) States within 0.05 eV of the top of the VB are strongly localized; lower energy states are quasidelocalized. (iii) The top two VB states have an almost identical degree of localization, with each state localized around two centers separated by about 7–15 BL. It is suggested that the electronic states in systems of randomly stacked layers may be studied experimentally. More detailed calculations involving various types of stacking faults embedded in D-Si layers and a full analysis of states other than at the top of the VB will be presented elsewhere.

The work at University of Missouri—Kansas City (UMKC) is supported by the U.S. Department of Energy under Contract No. DE AC02-79ER10462 and UMKC Research Council. The work at the University of Wisconsin—Madison is supported by the National Science Foundation.

*On leave from the University of Science and Technology of China, Hefei, People's Republic of China.

[1]For a detailed review see, for example, D. Thouless, in *Ill-Condensed Matter,* edited by R. Balian, R. Maynard, and G. Toulouse (North-Holland, Amsterdam, 1979), Vol 31. See also, M. Y. Goda, Suppl. Prog. Théor. Phys. 72, 232 (1982).

[2]C. J. Lambert and M. F. Thorpe, Phys. Rev. B 27, 715 (1983); M. Ya Azbel and P. Soven, *ibid.* 27, 831 (1983); A. D. Stone, D. C. Allan, and J. D. Joannopoulos, *ibid.* 27, 836 (1983).

[3]C. Kittel, *Introduction to Solid State Physics,* 5th ed. (Wiley, New

York, 1976), p. 28.
[4]W. Y. Ching and C. C. Lin, Phys. Rev. B 12, 5536 (1975).
[5]M.-Z. Huang and W. Y. Ching, Solid State Commun. 47, 89 (1983).
[6]K. L. Shaklee and R. E. Nahory, Phys. Rev. Lett. 24, 942 (1970).
[7]D. R. Hamann, Phys. Rev. Lett. 42, 662 (1979); C. S. Wang and B. M. Klein, Phys. Rev. B 24, 3393 (1981); M. T. Yin and M. L. Cohen, *ibid.* 26, 5668 (1982).
[8]R. S. Mulliken, J. Chem. Phys. 23, 1833 (1955).
[9]Because of the one-dimensional stacking sequence, the calculation on the D-Si supercell actually involved 204 layers.
[10]See, for example, I. L. F. Ray and D. J. H. Cockayne, Philos. Mag. 22, 853 (1979); L. C. Kimmerling, H. J. Leamy, and J. R. Patel. Appl. Phys. Lett. 30, 217 (1977); O. L. Krivanek and D. M. Maher, Appl. Phys. Lett. 32, 451 (1978).
[11]T. Y. Tan, H. Foll, and S. M. Hu, Philos. Mag. 44, 127 (1981).