Schottky Barriers without Midgap States*

Walter A. Harrison
Applied Physics Department, Stanford University, Stanford, California 94305
(Received 12 April 1976)

It is found that modification of the surface reconstruction on clean silicon surfaces could automatically bring the Fermi energy at the surface to midgap. The mechanism does not depend upon the existence of surface states in the gap. The corresponding effect is not expected on polar semiconductor surfaces.

Bardeen[1] first proposed that the pinning of the Fermi energy at midgap in semiconductors and the resulting Schottky-barrier formation arose from surface states. This has seemed plausible since dangling hybrid states might be expected to occur there. Indeed surface states appear to have been seen on silicon[2-4] and group III-V compounds[5] though there is evidence that the surface states can be different when a metal overlayer is applied.[6] The role of the surface states in the pinning remains uncertain.

The theoretical status of the problem is complicated by some uncertainty as to the nature of the surface. A recent attempt[7] to calculate surface reconstruction on clean surfaces concluded that the (2×1) reconstruction on a silicon (111) surface consists of *large* displacements which drop alternate dangling hybrids deep into the valence band and raise the others near to or into the conduction band. This does not preclude the existence of states in the gap since the reconstruction might well pull back-bond states into the gap. It suggests however that calculations on unreconstructed surface or weakly reconstructed[8,9] surfaces may not be relevant to experiment. Pandey and Phillips[10] also indicated large displacements on the basis of the experimental spectra, and noted the importance of back-bond states; this again casts doubt on the relevance of calculations based upon weak reconstruction, and suggests uncertainty in the nature of any surface states as well as their role in Fermi energy pinning.

In the present study we show that pinning is to be expected on clean surfaces of homopolar semiconductors whether or not there are any surface states at all in the gap. This is consistent with the universally observed pinning in homopolar semiconductors and with the recently observed lack of pinning on GaP surfaces.[11] It does not imply that surface states never participate in pinning, but only that the existence of pinning does not necessarily imply the presence of surface states at the Fermi energy.

The driving force for the reconstruction was the dehybridization energy which would be a very small effect if the dangling hybrids were singly occupied, but becomes very large after the electron transfer. In a pure (intrinsic) semiconductor, half of the dangling hybrids go each way leaving a neutral surface and no band bending. In an n-type semiconductor, on the other hand, a considerable dehybridization energy would be gained by placing two electrons from the conduction band in one of the empty dangling hybrid states and reversing its reconstruction to drop that level deep into the valence band. In fact, the energy gained is greater than that for the intrinsic case by an energy per pair equal to the band gap. This gain would be reduced by electrostatic contributions due to breaking the alternating pattern of reconstruction, but presumably the (2×1) reconstruction is broken into domains in any case and adding the extra charges at the domain boundaries would not cause a serious change in electrostatic energy. The net effect is to leave the surface negatively charged, raising the bands at the surface. Similarly in a p-type semiconductor we would expect a doubly occupied hybrid to give its electrons to the valence band, reverse reconstruction, and move up near the conduction band. In either case the process should continue until there are negligible numbers of electrons or holes, fixing the Fermi energy at midgap.

This effect need not be disrupted by surface contamination. For example, atomic oxygen is expected to chemisorb to the surface without modifying the neutrality of the surface of pure semiconductors.[7] Similarly, it would not modify the charging of the surface on a doped semiconductor, leaving the pinning as is. There is at work the same general effect which tends to sweep states from the gap in amorphous semiconductors; the system rearranges or deforms to drop the energy of occupied states and raise that of empty states. However, one could imagine that adsorbed hydrogen, for example, might saturate the dangling hybrids sufficiently stably to prevent any Fermi energy pinning; that seems uncertain.

The situation on polar semiconductors is quite different. On the (110) surface of gallium arsenide the arsenic atoms are expected to move outward with doubly occupied hybrids and the gallium atoms to move inward with empty dangling hybrids.[7,12] The counterpart of the modification of reconstruction given above for n-type silicon would be the outward movement of a gallium atom and the double occupation of its dangling hybrid. The considerably lower electronegativity of the gallium would work against this and would seem to explain the observed lack of pinning on clean gallium phosphide surfaces.[11]

This discussion does not argue against the existence of surface states in the gap, but only indicates that they are not necessary to an understanding of pinning.

The author is indebted to J. Van Laar and W. E. Spicer for discussions of this problem.

*Supported by in part by National Science Foundation Grant No DMR73-02351 and in part by Advance Research Projects Agency of the Department of Defense and monitored by Night Vision Laboratory, U. S. Army Electronics Command, under Contract No. DAAK 02-74-C-0069.

[1]J. Bardeen, Phys. Rev. 71, 717 (1974).

[2]G. Chiarotti, S. Nannarone, R. Pastore, and P. Chiaradia, Phys. Rev. B 4, 3398 (1971).

[3]A. Deneuville and B. K. Chakraverty, Phys. Rev. Lett. 28, 1258 (1972).

[4]L. F. Wagoner and W. E. Spicer, Phys. Rev. Lett. 28, 1381 (1972).

[5]D. E. Eastman and J. L. Freeouf, Phys. Rev. Lett. 34, 1624 (1975).

[6]J. E. Rowe, S. B. Christman, and G. Margarito, Phys. Rev. Lett. 35, 1471 (1975).

[7]W. A. Harrison, Surf. Sci. 55, 1 (1976).

[8]J. A. Appelbaum and D. R. Hamann, Phys. Rev. B 12, 1410 (1975).

[9]M. Schlüter, J. R. Chelikowsky, S. G. Louie, and M. L. Cohen, Phys. Rev. Lett. 34, 1385 (1975).

[10]K. C. Pandey and J. C. Phillips, Phys. Rev. Lett. 34, 1450 (1975).

[11]P. W. Chye, I. A. Babalola, R. Sukegawa, and W. E. Spicer, Phys. Rev. Lett. 35, 1602 (1975).

[12]This conclusion has been recently confirmed in calculations by A. R. Lubinsky, C. B. Duke, B. W. Lee, and P. Mark, Phys. Rev. Lett. 36, 1058 (1976).

ERRATA

CONJECTURE ON MAXIMAL VIOLATION OF T INVARIANCE IN DILEPTON PRODUCTION BY NEUTRINOS. Robert G. Sachs [Phys. Rev. Lett. 36, 1014 (1976)].

The statement to the effect that correlations between the incident neutrino momentum and either the momenta or the spins of the two charged leptons provide tests of T invariance must be qualified since final-state interactions of the superstrange hadron can also lead to such correlations through decay of the hadron into one of the leptons. Therefore the occurrence of such correlations would have an ambiguous interpretation in the absence of further information about the ss hadron interaction. This error was called to my attention by E. Derman [see footnote 9 of L. N. Chang, E. Derman, and J. N. Ng, Phys. Rev. Lett. 35, 6 (1975)].