Dangling Bonds and Dislocations in Semiconductors*

VOLKER HEINE†
Department of Physics and Institute for the Study of Metals, University of Chicago, Chicago, Illinois
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Experimentally, dislocations in germanium have a negative core charge due to the filling of some acceptor states. These states do not appear to be related directly to "dangling bonds," since the charge is similar in screw and edge dislocations. A one-dimensional model is investigated in which a small amount of free volume, to represent the core of the dislocation, is inserted into a ring of N atomic potentials. In this model it is found (a) there is a localized state in the gap; (b) it is pulled out of the upper "conduction" band, in agreement with the sign of the core charge; (c) the localized state exists whether there are bonding states below the gap and antibonding above, or vice versa, and thus is not related to the Shockley condition for a surface state; (d) the cause of the extra state is the local decrease in atom density.

IT is well known that dislocations in group-IV semiconductors carry a charge in the core,[1,2] resulting in a bending of the bands for a large distance around, as shown in Fig. 1. In recent years the picture has been established very precisely through growing regular nets of known dislocations in the form of low-angle grain boundaries.[3–10] Figure 1 shows the situation in Ge (n-type), the dislocation having a negative charge.

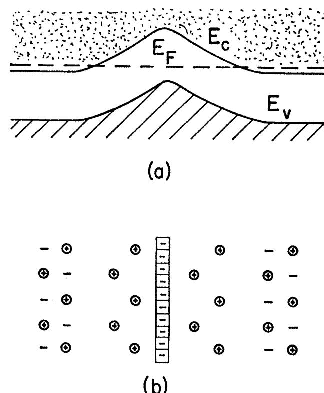

FIG. 1. (a) Bending of bands around a dislocation in n-type Ge. Shown are the top of the valence band E_v, bottom of the conduction band E_c, and Fermi level E_F. (b) The charge density in the same region. Ionized donors are enclosed in circles, the charges on the dislocation in squares, and the mobile carriers are shown free. The width of the space-charge region is typically 10 000 Å.

Sometimes the band bending is sufficiently strong that the peak of the valence band rises above E_F, resulting in a narrow "inversion layer" of positive holes perhaps 20 Å wide around the dislocation core.[6–8]

The previous explanation of the behavior has been as follows.[2] In the core of the dislocation, some covalent bonds between atoms are broken, and it was suggested that this could result in local acceptor states analogous to surface states. These states have often been thought of as highly localized[1] electron states sited at the "dangling bonds."

There are, however, severe difficulties with any literal interpretation of such a picture. It is found that in Ge the negative core charge exists equally on edge dislocations where there may be broken bonds, and on screw dislocations where there are none.[5,11] This is similar to the situation with surface states, where the observed insensitivity of surface properties argues strongly against surface states having the character of dangling bond states.[12] Moreover, to get a net negative charge in the dislocation core, one has to pull the localized states out of the conduction band: States split off from the valence band do not contribute to the net negative charge since the total number of states in the band and split off from it is conserved.[13] All the conduction-band states are antibonding, so that one wonders how appropriate it is to refer to such localized states pulled out of it as dangling "bonds."

The purpose of the present note is to shed some light on this rather confused situation from a one-dimensional analog. We consider a ring of N cells (N even) of length a with an insertion of width $2b$ ($2b<a$) somewhere between two cells (Fig. 2). The insertion represents the

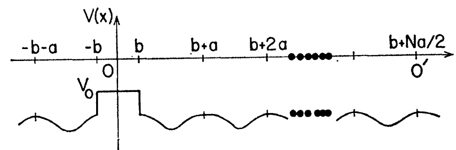

FIG. 2. One-dimensional periodic potential with an insertion of width $2b$ and potential V_0.

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† Permanent address: Cavendish Laboratory, Free School Lane, Cambridge, England.
[1] See, for example, W. T. Reed, Phil. Mag. **45**, 775 (1954); Solid State Phys. **1**, 283 (1955).
[2] W. Shockley, Phys. Rev. **91**, 228 (1953).
[3] See Refs. 4 to 10 for typical studies and more complete references.
[4] H. F. Matare, B. Reed, and O. Weinreich, Phys. Rev. **113**, 454 (1959); R. K. Mueller, J. Phys. Chem Solids **8**, 157 (1959).
[5] R. K. Mueller, J. Appl. Phys. **32**, 640 (1961).
[6] R. K. Mueller, J. Appl. Phys. **30**, 2015 (1959).
[7] G. Landwehr and P. Handler, J. Phys. Chem. Solids **23**, 891 (1962).
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[10] G. L. Pearson, W. T. Read, and F. J. Morin, Phys. Rev. **93**, 666 (1954).
[11] J. Hornstra, J. Phys. Chem. Solids **5**, 129 (1958).
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[13] P. Handler and W. M. Portnoy, Phys. Rev. **116**, 516 (1959).

extra space in the center of the dislocation. We choose the potential V_0 there to be above the bottom of the band (which is equal to the mean pseudopotential in the solid) but below the band gap. This must correspond to the situation in Ge where the valence-band width is of the order of 1 Ry and the variation of the pseudopotential in the regular solid about its mean only 0.2 Ry.[14] We consider in our model the states near the first band gap at $k=\pi/a$ of the regular solid in the nearly-free-electron approximation,[15] and choose the $2\pi/a$ Fourier component of the pseudopotential to be positive corresponding to a bonding p-like state E_p at the top of the first band and an antibonding s-like state E_s at the bottom of the second band. We choose as origin $x=0$ the center of the insertion. All states are either even or odd about the origin 0, and automatically also about the point $x=b+\frac{1}{2}Na$ (the "anti-origin" 0') half-way round the ring. In the limit $b=0$ it may easily be verified that there are $\frac{1}{2}N+1$ even states in the first (or "valence") band, including one at E_p, and $\frac{1}{2}N-1$ odd states. The next odd state lies at the top of the gap at E_s.

In the solid, the wave functions must be linear combinations of the Bloch states ψ_k, ψ_{-k}, and by matching these onto cosine or sine functions in the insertion with a nearly-free-electron approximation, there is no difficulty about following what happens to the energy levels in detail. However all the results we require can be obtained by counting nodes and using the theorem that the number of nodes increases by one between consecutive states.

We have to deal with real wave functions, treating even and odd states separately. At the energy E_p, we can start integrating at 0' an even state with $d\psi/dx=0$, and obtain a phase of $\frac{1}{2}N\pi$ on going half-way round the ring to $x=\pm b$: Then since $V_0<E_p$ we pick up an extra positive bit of phase on going through the insertion to 0. Thus the $(\frac{1}{2}N+1)$th even state has energy slightly below E_p and there are $\frac{1}{2}N+1$ even states in the valence band as for $b\equiv 0$. Similarly we find $\frac{1}{2}N$ odd states below E_s. Since for $b=0$ there are only $\frac{1}{2}N-1$ odd states in the valence band, we expect from continuity one of the odd states to be a localized dislocation state in the band gap, which is pulled out of the conduction band as b increases from zero. That this is so can be seen explicitly by integrating an odd state from 0, leading to a positive value for $(d\psi/dx)/\psi$ at $x=b$, which is just the condition needed[16] for a localized state exactly as in the case of Shockely "surface" states. The anti-origin is sufficiently far away for the matching condition there to make only an infinitesimal difference.

The result is likely to be valid also in three dimensions. Near a band edge one can do an expansion in angular momenta and radial wave functions. The Shockely condition will give a localized state in the $l=0$ wave. The relevant band gap is the gap in a two-dimensional section of the band structure at constant k_z, where k_z is the wave vector parallel to the dislocation. The localized states would form a band in k_z of one state per unit lattice periodicity along the dislocation, and part of this band can lie below the absolute maximum of the valence band. Thus the Fermi level may come above or below the top of the valence band according to detailed circumstances, as found in practice.

We conclude that localized around a dislocation there is a band of states pulled out of the *conduction* band. The core of a dislocation is presumably an energetically less favorable place for an electron to be, compared with being in the bonds as the valence states are. The core therefore appears in a sense as a repulsive perturbation, and it may seem surprising that it pulls states out of the *bottom* of a band. However the extra space represented by the core allows all the states to spread out more, thus lowering the de Broglie wavelength and hence the energy levels. The relevant criterion therefore is that V_0 be less than the energy at the gap. In the usual effective-mass approximation, we can represent an electron in the conduction band as a plane wave $\exp i\mathbf{K}\cdot\mathbf{r}$ where $\mathbf{K}$ is measured from the band minimum, and the mean effective potential it sees inside an atomic cell is equal to the bottom of *that* band, i.e., the conduction band in our case. In comparison the V_0 inside the open space in the core of the dislocation is a deep potential well. In two dimensions perpendicular to the dislocation, such a perturbation always produces a bound state,[17] as in one dimension. As in the case of surface states, the lateral dimension of any state in the band gap is several atomic diameters,[12] certainly not as localized as one bond.

In our model above, the localized dislocation state was similar to a Shockley surface state, and its existence related to the Shockley condition of bonding states below the gap and antibonding above. However the same argument of node counting shows that we get a similar state in the gap if E_s and E_p are reversed, the antibonding state being below the gap. We conclude that the existence of the dislocation states is not necessarily associated with the Shockley condition or/and the existence of a broken bond. They are simply caused by the extra bit of space and V_0, and we therefore expect screw dislocations without broken bonds to have dislocation states as well as edge dislocations.

Finally as regards InSb, the theoretical situation is unchanged, as recognized by Holt[18] but not all writers. The pseudopotentials of the two atoms are really quite similar,[19] and provided equal numbers of In and Sb

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[19] M. L. Cohen and T. K. Bergstresser, Phys. Rev. **141**, 789 (1966).

atoms are removed in taking away one lattice plane to form the dislocation, we expect a negative dislocation charge as in Ge. However a positive core charge is found[8,9,20] experimentally, at least in low-angle grain boundaries grown from the melt. The explanation we suggest is that excess Sb atoms are grown in substitutionally near the core during crystallization, and more work on dislocations produced by plastic deformation would therefore be of interest. At the grain boundary during growth there will be dipolar electric fields alternating in sign as the crystal grows. There is therefore no net attraction of In or Sb atoms due to their charge, but the field gradient would preferentially attract Sb atoms since these will be somewhat larger, "softer," more polarizable.

In silicon a positive core charge has also been reported,[21] which cannot, of course, be explained by the mechanism suggested for InSb. It is presumably due to other causes than those considered in the present paper. However, it should be noted that in our theory, the removal of some volume, or what is the same thing, a local excess atom density, will lead to the repulsion of levels out of the valence band and, hence, a positive core charge. Now the diamond structure is of course very open, and germanium for instance shrinks on melting. It is therefore not impossible, though unlikely, that the atom density in the disordered region in the core of the dislocation is somewhat higher than in the bulk, accounting for a positive core charge in silicon.

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High-Energy Emission in GaAs Electroluminescent Diodes

M. I. NATHAN, T. N. MORGAN, G. BURNS, AND A. E. MICHEL
IBM Watson Research Center, Yorktown Heights, New York

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A study of high-energy photon emission ($h\nu - eV \gg kT$) from various GaAs diodes is reported and the results analyzed. We find that this emission is produced by most diffused diodes except those doped with Sn and Ge. It is not observed in solution-grown diodes, no matter what the doping. It is always accompanied by a large amount of excess (nonradiative) current and can be explained in terms of the Auger recombination of carriers at defects with subsequent diffusion of the excited electrons to the p side of the junction.

INTRODUCTION

DURING the past few years considerable work has been done on the electroluminescence of forward-biased GaAs diodes at wavelengths near the absorption edge. This work has been directed toward experimentally characterizing the electro-luminescence and identifying the various recombination mechanisms involved. Pankove[1] reported that the emission line near the edge, which gives rise to the laser action at high current densities, shifts to higher photon energy with increasing current. He attributed his results to tunneling with photon emission. Shortly afterward a correspondence between this edge electroluminescence and the photoluminescence of homogeneously doped p-type samples was reported, indicating that an acceptor is involved in this transition.[2]

Subsequently it was found that the shift reported by Pankove resulted from a tendency of the low-energy side of the line to saturate and the high-energy side of the line to increase super-linearly with current.[3,4] It was also found by Nelson *et al.*[3] that the photon energy of the peak of the line $h\nu_1$ satisfied

$$h\nu_1 = eV + \delta E, \tag{1}$$

over a range from 1.3 to 1.5 eV, where V is the applied voltage and δE is a small correction (a few meV) which depends on temperature. It was suggested[3,4] that the shift was caused by a filling up of an exponential tail on the conduction band density of states which comes about as a result of the high density of impurities and/or mobile carriers. Archer *et al.*[5] found that Eq. (1) holds for applied voltages as small as 1.1 V. In the voltage range from 1.1 to 1.3 V these workers presented evidence for tunneling into the forbidden gap with photon

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