

NEW PHENOMENON IN SEMICONDUCTOR JUNCTIONS—GaAs DUPLEX DIODES*

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(Received 27 July 1970)

By the introduction of a deep center, a "polarizable" GaAs junction has been obtained which exhibits duplex or multiplex stable dc current-voltage characteristics. Each conduction state, "polarized" by a characteristic threshold voltage, appears to last indefinitely with low applied voltages at room temperature. This effect can be explained by assuming that the deep center, consisting of oxygen possibly in combination with other impurities, possesses an inherent bistability.

A semiconductor junction may be identified by a space-charge layer or a dipole layer which depends upon ionized impurity distribution and applied voltages across the junctions.

In diffusing oxygen into GaAs, we have found a deep center which acts as if it has a bistability over the temperature range 230 to 380°K, where its two stable states have different electronic charges. By forming the deep centers in addition to normal shallow impurities in the space-charge region, we have obtained a junction "polarizable" with forward and reverse applied voltages exceeding certain threshold values. The junction capacitance at the same voltages varies between two extremes C_1 and C_2 . Although the capacitance change is only about 1%, polarization has profound influence on the transport properties of the junction and also affects its optical properties.

The junctions have been fabricated by different methods. Typically, oxygen was first diffused at 500~600°C for several minutes into n -type GaAs ($10^{16} \sim 10^{17} \text{ cm}^{-3}$), then an electrode metal such as In-Zn alloy, etc., was evaporated and the specimens were subsequently subjected to short-period heating at 700~800°C. The latter resulted in shallow alloying of the metals and diffusion of the constituents involved. During the fabrication process, a number of deep centers,¹ some of which have the aforementioned bistability, are created by oxygen,² possibly in combination with other impurities³ or vacancies or defects.

The typical characteristics at room temperature are illustrated in the lower part of Fig. 1 together with plots of $(\text{capacitance})^{-2}$ versus applied voltage. The device, referred to here as a duplex or multiplex diode, exhibits two or more stable dc current-voltage curves.⁴ The dashed curve, which represents the low-conductive state, is switched to the solid curve of the high-conductive state at a forward threshold bias, as shown by an arrow from A to B. Transition back to the low-conductive state occurs

at a reverse threshold bias from C to D or from c to D via d. Thus the high- and low-conductive states may be thought of as forwardly and reversely "polarized" states (FP and RP), respectively. It should be emphasized that either state appears to last indefinitely at low applied voltages; units stored for a few weeks at room temperature remained in their original states.

The plots of $(\text{capacitance})^{-2}$ versus applied voltage over a limited bias range show a straight line for each state and its slope agrees approximately with the original donor concentration, indicating that the unit is essentially a p^+-n junction. These straight lines, however, intersect the abscissa at values higher than the built-in voltage, giving a space-charge width at zero

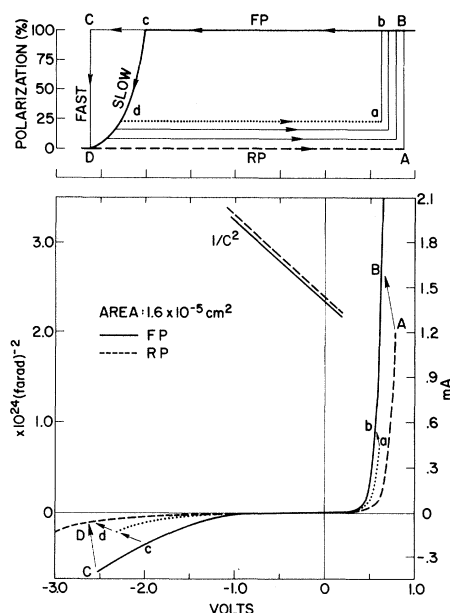


FIG. 1. Lower part: typical duplex or multiplex current-voltage characteristics with plots of $(\text{capacitance})^{-2}$ versus applied voltage at room temperature. The dotted line indicates one of the intermediate states and the arrows show transition paths between states. Upper part: hysteresis loops of "polarization" as a function of applied voltage for the same unit.

bias wider by several hundred angstroms than that expected from the original donor concentration. The measured capacitance of the FP state is about 1% larger than that of the RP state at the same bias voltages.

By analogy with ferroelectricity, hysteresis loops of polarization as a function of applied voltages can be derived from fast- and slow-scanned measurements, as shown in the upper part of Fig. 1. They correspond to the current-voltage characteristics in the lower part, where the abscissa is common. First of all, a degree of polarization is estimated from capacitance as well as conductance measurements. The RP and FP states are chosen to be zero and 100% in polarization, respectively. Now, starting at *B* or *b* in the FP state and following the direction indicated by arrows, one sees that switching occurs at *c* or *C*, depending upon the speed of voltage sweep. Vertical lines indicate that polarization or depolarization proceeds rapidly. The unit reaches a saturation at *D* with no further polarization. The magnitude of polarization is primarily determined by the highest reverse-bias voltage attained without forward switching and is not changed for subsequent decreased voltages, as shown by horizontal lines. Following each arrow (going to the right), one sees a transition back to the FP state at *a* or *A*, depending upon its polarization. The FP state is unchanged with further increase in forward bias.

The reverse switching of *C-D* or *c-d* usually follows a simple exponential decay whereas the forward switching of *A-B* is preceded by a delay time. The total switching times for the former and the latter were measured, for instance, to be 400 μsec and 200 μsec , respectively, although these time constants depend very strongly on the applied pulse amplitude. In slow-scanned measurements, the time constants can be as long as 1 sec.

The forward current, as shown in Fig. 1, can be described by an $\exp(eV/nkT)$ dependence, where n is 1.5-3 and is smaller for the FP state. This implies that the recombination current dominates conduction for both states. The current J can be given, using a simplified model,⁵ by

$$J = J_0 \exp\left(\frac{eV - E_g}{2kT}\right),$$

where E_g is the energy gap and n is assumed to be 2. Therefore, the voltages V_{FP} and V_{RP} at a given current J_1 , corresponding to the FP and RP states, respectively, are given as a function

of temperature by

$$E_g - eV_{\text{FP or RP}} = 2kT \ln(J_0/J_1),$$

where J_0 is a function of polarization and varies slowly with temperature. We have made measurements on these voltages at $J_1 = 1$ mA over the temperature range 200 to 400°K, indicating that both V_{FP} and V_{RP} decrease linearly with increase in temperature, as shown in Fig. 2. There are two critical temperatures: 234 and 376°K. Approaching these temperatures, one state becomes increasingly unstable and finally the RP and FP states disappear below 234°K and above 376°K, respectively. There are also minor anomalies at these temperatures as indicated by arrows in Fig. 2. Similar experimental results for several units show that these critical temperatures are $230 \pm 10^\circ\text{K}$ and $380 \pm 10^\circ\text{K}$. In other words, the stable and metastable ground states are inverted with temperature. This observation seems to indicate that the deep center involved here has low- and high-temperature phases and its bistability is exhibited only over an intermediate temperature range.

The observed increase in capacitance, ΔC , in the transition from the RP state to the FP state may be explained if we assume that the centers become more positively (or less negatively) charged, possibly by trapping injected holes, thus the space-charge width is narrowed due to an increase, ΔN , in the effective donor concentration N . Since C is proportional to \sqrt{N} ,

$$\Delta N \sim 2N(\Delta C/C) \sim 8 \times 10^{14} \text{ cm}^{-3}$$

for the unit shown in Fig. 1. This more positively charged state of the center, which corresponds

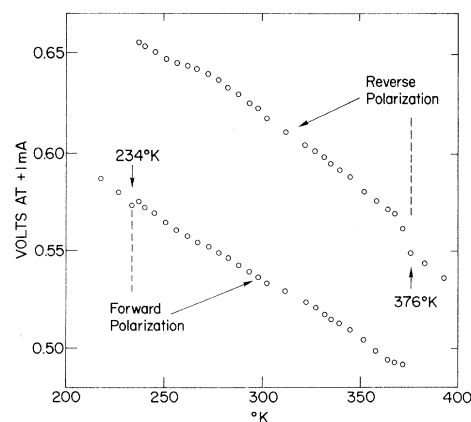


FIG. 2. The voltages V_{FP} and V_{RP} at +1 mA, corresponding to the FP and RP states, respectively, over the temperature range 200 to 400°K.

to the low-temperature phase, is considered to have a larger cross section in the electron-hole recombination-generation process than the other state. This change would then lead to a considerably different voltage dependence of the recombination current which, we believe, is primarily responsible for the observed duplex or multiplex characteristics.

It should be recognized that, in our proposed mechanism, a hole is captured by the center in two different ways; one is that a hole entering the center changes its structure and the other is that a hole orbiting the center recombines eventually with an electron.

We have made measurements on the spectral photoresponse of the junction for the FP and RP states over the photon energy range 0.8 to 1.6 eV. No difference was observed in the high-energy range for both states and during the measurements there was no evidence of the transition from one state to the other. Figure 3 shows semilog plots of photovoltage versus photon energy with no external bias voltage for both states at room temperature, indicating broad structure at energies below the band edge. In this photon energy range, the FP state always showed a higher photosensitivity, which probably supports our proposal that this state has a larger cross section in the recombination-generation process than the RP state. Two broad peaks in the FP state are located at slightly higher energies than the corresponding two peaks in the RP state. This may indicate that each state of the center

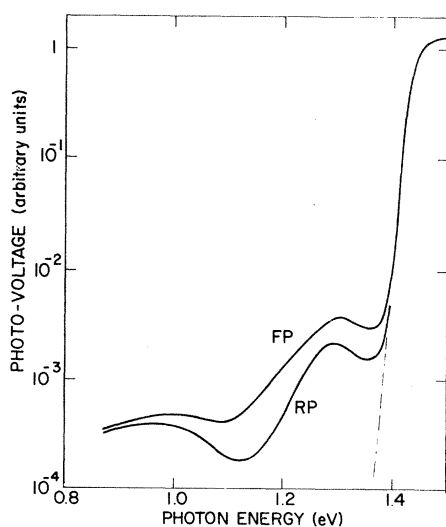


FIG. 3. Semilog plots of photovoltage versus photon energy for the FP and RP states with no externally applied bias voltage.

has its own characteristic energy level.

We believe that the transitions occur spontaneously with increasing electric field strength in the reverse-biased junction and with increasing injected electron and hole concentrations in the forward-biased junction. Therefore, it is possible that with higher reverse-bias voltages, more centers become involved in this effect, resulting in a higher degree of reverse polarization. In the forward direction, however, once switching starts at point *A*, it will be accelerated because of increasing injected carriers, going rapidly to point *B*, just like the current-controlled negative resistance. The transition involved here may not be purely electronic. With the electronic configuration change, the center may rearrange its structure, including a repositioning of the lattice site and a changing of the magnitude and the direction of the lattice distortion.

We have observed a similar duplex effect with GaAsP crystals and much less prominently with Si crystals. To our knowledge, this type of long-lived effect in monocrystalline GaAs or Si junctions at 300°K has never been reported. Recently Holonyak et al.⁶ observed, in their GaAs tunnel diodes, that electrical or optical injection could alter the ground state of the Au trap. This process, according to them, creates quasistable Au levels which apparently last for over 1 h at 77°K. The photosensitivity of our device at photon energies of the band-to-band transition seems no greater than that of regular semiconductor junctions, although under illumination the *A-B* and *C-D* switching thresholds are found to decrease. We believe that, if the electron-spin-resonance technique could successfully be applied here,⁷ it would greatly help in understanding the structure of the center.

The authors are grateful to V. Leo Rideout for stimulating discussions and to Leo Alexander for his excellent assembly work.

*Research sponsored in part by the Army Research Office (Durham) under Contract No. DAHCO4-69-C-0069.

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²W. J. Turner, G. D. Pettit, and N. G. Ainslie, *J. Appl. Phys.* **34**, 3274 (1963).

³No specific effort was made to prevent Cu diffusion.

⁴In measuring more than 50 units assembled, the dc power required for transitions ranged from 1 to 20 mW,

with lower power being required for the forward transition. Since the finished unit, which had a heat sink, usually could stand power dissipation of more than a few watts without noticeable change, the effect is not likely to involve heating, melting, or crystallization of materials involved. Since the above-described fabrication process for GaAs crystals of more than 10^{18} cm^{-3} donors provides nearly normal p - n junctions with

In-Zn alloy, we do not think any oxide layers are involved in the observed effect.

⁵C. T. Sah, R. N. Noyce, and W. Shockley, Proc. IEEE **45**, 1228 (1957).

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⁷See, for instance, G. W. Ludwig and H. H. Woodbury, Solid State Phys. **13**, 223 (1962).

LINEAR COMBINATION OF ATOMIC ORBITAL-MOLECULAR ORBITAL TREATMENT OF THE DEEP DEFECT LEVEL IN A SEMICONDUCTOR: NITROGEN IN DIAMOND

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(Received 11 June 1970)

A deep defect level in a semiconductor is simulated by a large cluster of host atoms surrounding the defect. The electronic states of the entire system are then computed by linear combination of atomic orbital-molecular orbital techniques. The nitrogen donor in diamond is treated as an example. A large Jahn-Teller distortion is predicted which forces the donor state down close to the valence band, in good agreement with experiment. The calculated donor wave function agrees with EPR and electron-nuclear double resonance results.

The effective-mass treatment of Kohn and Luttinger¹ has been highly successful in describing the electronic structure of shallow impurity states in semiconductors. However, this approach has not been successful for defect states which are located more than ~ 0.1 eV from the band edges. A satisfactory theoretical treatment of the deeper levels has not been given and poses one of the central unsolved theoretical challenges in solid-state physics.

In this Letter we describe a possible approach to the problem using molecular-orbital (MO) techniques. We consider a large molecule made up of the defect and a sufficient number of host-atom neighbor shells surrounding it to constitute a small "crystal." The electronic states of the entire system are then computed by using an approximate linear combination of atomic orbital-molecular orbital (LCAO-MO) method on a high-speed electronic computer.

As a model calculation, we consider the 35-carbon-atom diamond lattice shown in Fig. 1. For the present calculation extended Huckel theory² (EHT), which is a simple one-electron molecular-orbital treatment, has been used. The EHT method may be characterized briefly as follows:

- (1) The MO's, φ_i , are represented as $\varphi_i = \sum_v c_{vi} \chi_v$, where χ_v is an atomic orbital.
- (2) The solution of the secular equations $\sum_v (H_{\mu\nu} - E_i S_{\mu\nu}) c_{vi} = 0$ yields the MO energies E_i and

the MO coefficients c_{vi} . $S_{\mu\nu}$ are the overlap matrix elements, and $H_{\mu\nu}$ the matrix elements of an effective one-electron Hamiltonian H .

(3) $H_{\mu\nu} = \frac{1}{2}K(H_{\mu\mu} + H_{\nu\nu})S_{\mu\nu}$, $H_{\mu\mu} = -I_\mu$, where the I_μ are taken as the empirical atomic ionization energies.

The atomic orbitals are taken to be one 2s and three 2p Slater orbitals on each carbon atom (orbital exponent, 1.625); the I_μ used are 19.44

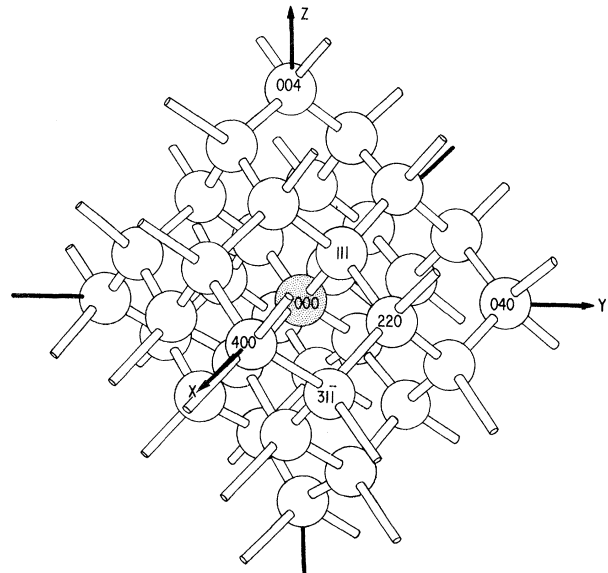


FIG. 1. The 35-atom cluster used for the LCAO-MO calculations.