

FIG. 3. Potentials measured by a set of superconducting and normal probes situated within $3 \mu\text{m}$ of a current-carrying S/N boundary. Note that the potential of the superconducting lead is *higher* than that of the normal lead.

below 3.99°K as it does.

A confirming test involved putting a superconducting voltage lead in between the S/N interface and the normal lead. The leads, each slightly less than $1 \mu\text{m}$ wide and separated by $1 \mu\text{m}$ from each other, were situated as close as possible to the interface such that the outermost edge of the normal voltage probe was about $3 \mu\text{m}$ away from the interface. The geometry is shown in the in-

set in Fig. 3. When the whole film was normal, a resistive potential drop was developed across the two probes as indicated to the right of Fig. 3. However, just below the superconducting transition, this voltage *reversed* in polarity. This we take as additional evidence that the quasiparticles are being subjected to an electric field even though they are relatively far from the boundary, and have a lower chemical potential than the pairs near the boundary.

Most of these results agree with the predictions of the theory.¹ However, the effective coherence length is larger than expected³ in this thickness-limited situation, possibly implying further non-equilibrium effects.

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Electronic Basis of Switching in Amorphous Semiconductor Alloys

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Reversible threshold switching in the amorphous covalent alloys is explained by the carrier transport and recombination properties of the "relaxation semiconductor," defined by dielectric relaxation time greater than recombination time. In these alloys, the recombination after single free paths pins the Fermi level at the location for minimum conductivity. Characteristic "recombinative injection" of minority electrons is the final process in the switching, and it accounts for observed behavior in its various aspects.

This Letter explains on an electronic basis the reversible threshold switching in amorphous semiconductor alloys^{1,2} and presents a related new approach to understanding these materials. The alloys are examples of the *relaxation semiconductor*,³ which is defined by⁴ dielectric relaxation time greater than recombination time or *diffusion-length lifetime*^{5,6} τ_0 . The defining condition has a drastic and fundamental influence on the transport⁴ and on the trapping and recombina-

tion properties. It leads characteristically to *recombinative space-charge injection* or, more briefly, *recombinative injection*. This is a type of minority-carrier injection predicted by the theory,^{7,8} confirmed by experiment,⁷⁻⁹ and proposed as a unifying principle for various electronic switching and charge-storage effects.¹⁰

First, an outline of the model: The alloys are *p* type and their switching is due to recombinative injection of electrons following a preswitching

range.¹⁰ In this range, carriers are activated by the field. The threshold is reached upon activation of nearly all localized holes. In the switched state, recombinative injection has produced a steady-state region of minority-carrier space charge in which recombination is just balanced by thermal generation. The net volume recombination rate \mathcal{R} is nonzero only at the end of this region, in a narrow *recombination front*⁷⁻⁹ at the anode.¹⁰ That reversible switching or no field breakdown in this front requires diodes shorter than a few micrometers implies that a moderate initial localized-hole concentration \hat{p}_0 of order $10^{17}/\text{cm}^3$ is activated and neutralized. This implication is accounted for. Theory for the recombination indicates that the amorphous alloys at equilibrium have equal electron and hole capture rates per unit volume with recombination after single free paths. Consequently, they have equal mean free paths and equal electron and hole conductivities, or minimum (*p*-type) conductivity for a given band gap.⁸ The Fermi level is so pinned simply by the recombination and not by large concentrations of ionized centers. In particular, the recombination occurs at energy levels of centers which are ionized in only moderate concentrations and nearly all neutral as a result of self-compensation. Such centers are in effect donors towards the valence band and acceptors towards the conduction band, and, with mobility edges,¹¹ they are the centers in fairly short band tails.

Consider now preswitching with the field-activated current density^{12,13}

$$I \approx [\sigma_c \exp(-\mathcal{E}/kT)] [\bar{E} \exp(eE\bar{l}/kT)], \quad (1)$$

$$E > \bar{E} = kT/e\bar{l},$$

that many of the alloys exhibit.¹³⁻¹⁵ Here σ_c is a conductivity roughly the same for most alloys, \mathcal{E} is an effective conductivity band-gap energy, and \bar{l} a characteristic length for the field dependence. The conduction process of Eq. (1) in the high-field range is the same as it is near equilibrium, the shape of a normalized current-voltage characteristic being independent of T . This observation^{13,14} is explained by the minimum-conductivity property: The electron and hole conductivities remain equal as carriers are activated by fields from the respective ionized centers. Hence single-free-path recombination still obtains, and \bar{l} is essentially the common mean free path; its observed value¹³⁻¹⁵ is at 300°K somewhat smaller than 10^{-6} cm, which is of order of an electron wavelength. For the fields of Eq. (1), energies

gained in a mean free path therefore exceed kT ; microscopic velocities increase slowly, about as $E^{1/2}$. Meanwhile, observed I increases by a factor¹⁴ exceeding about 20, an increase which must be largely due to activated concentrations. Threshold field, moreover, decreases with increase in T ; it extrapolates to zero¹⁴ at about 500°K. Further activation through temperature rise occurs during the characteristic switching delay time at the threshold.¹⁵ The holes are first to be completely activated, and then I cannot increase further by this preswitching mechanism.

Figure 1 shows an energy-band diagram for a region of injected electrons maintained by minimum holding current I_h between nonrectifying contacts, a *forward current* by convention. In this region of $\mathcal{R} = 0$ the product np of the concentrations retains its thermal-equilibrium value, so that the electrochemical potentials ϕ_n and ϕ_p for electrons and for holes have a common value, the *relaxation potential*⁸ ϕ_R . In the recombination front, ϕ_R separates into ϕ_n and ϕ_p as shown, and electron current changes to hole current in transit time of order τ_0 . In this case of reversible switching, the space charge in the diode under I_h self-consistently gives a largest field in the front equal to the threshold field E_h . If forward bias is reduced below the holding bias V_h , then the current decreases and some positive charge shifts externally to the cathode and reduces the space charge. The field in the front is then less than E_h and activates fewer carriers,

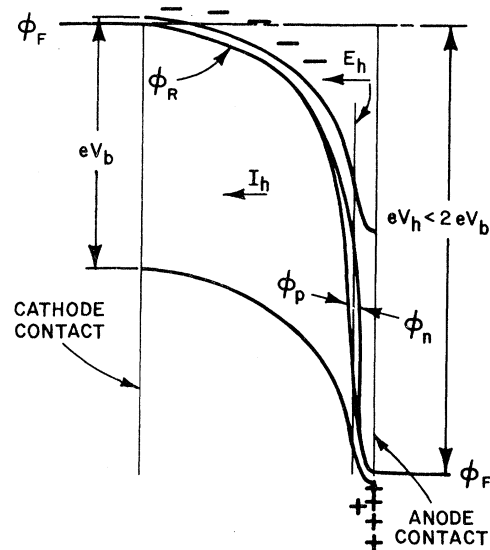


FIG. 1. Energy-band diagram for minimum holding current after recombination space-charge injection of electrons.

and a further decrease in current causes more positive charge to shift, and so on until the space charge is gone. An increase in forward current above I_h requires carrier injection. The electrons go mainly to the front, where velocities are largely saturated, so that any increase in current requires increased concentrations. The field is hardly increased in the front, which stabilizes readily through increases in n , p , and \bar{R} , with φ_n and φ_p moving towards the band edges. In this way, the injection results in a differential resistance \bar{R} which is small, positive, and substantially constant despite the varying cross section^{15,16} of the current path.

The model accounts further for observed behavior. The transit time under a microscopic electron velocity of 10^7 cm/sec, which is 10^{-11} sec for a length of 10^{-4} cm, should be a lower limit for the switching time, and this time is observed¹⁰ to be of order 10^{-10} sec. Induced space charges near the contacts before switching partially screen the field. Hence the injected charge reverses the space-charge polarization¹⁷ and observed^{14,18} differential capacitance goes negative at the threshold. Figure 1 shows V_h . The variation in potential from the large-signal space charge is a major fraction of the band-gap potential V_b , and the Fermi potential φ_F at the contacts lines up with φ_R . Hence V_h is somewhat larger than V_b but less than $2V_b$ and does not depend on length nor strongly on temperature. This is the holding voltage that is observed.^{15,16} Any growth after threshold switching of a conducting crystalline "lock-on memory" filament of modified composition is always from the anode¹⁹⁻²¹; most of the heating is in the recombination front, and electron injection^{10,21} puts this at the anode. Heating there has been shown by a scanning electron microscope.²¹ The "transient ON characteristic"²² is a definitive indication of the narrow front. This is current from a short probing pulse whose polarity and voltage V can be changed and which is applied shortly after reversible threshold switching. When $|V|$, regardless of polarity, is less than V_h , a high resistance, or the "blocked ON state," is observed, while V of either polarity with $|V| > V_h$ gives about the same differential resistance as in the steady state.²² The high resistance for $|V| < V_h$ is simply that of recombination fronts at both contacts with fields less than E_h ; one is reverse biased. The low and constant \bar{R} for $|V| > V_h$ is associated with a single front at the anode and the injection from the contacts. Reversal of polarity

of bias that gives low \bar{R} simply shifts the front rapidly from one contact to the other, showing the absence of an extended region¹⁷ of "space-charge overlap." Also, reported effects of polarity, duration, current, and voltage of the first of a pair of short pulses, as well as elapsed time, on switching by the second pulse permit distinction between electronic and thermal behavior and are consistent with switching by carrier injection.^{23,24} Concentration of centers well within the gap less than about $10^{17}/\text{cm}^3$ is indicated by optical data.^{25,26} Recombination at levels not far inside the mobility edges is consistent with photoconductivity and luminescence measurements.²⁷ Energy of activation $eE_h\bar{L} \approx 0.1$ eV gives the switching threshold.¹⁴

The ionized concentration $\hat{n}_0 \approx \hat{p}_0$ may be estimated from measurements²⁸ of the ac field effect in amorphous chalcogenide films. Considering the recombination, electrons scattered into and out of surface states will cause band bending by about a Boltzmann potential, with holes in a surface layer of about 10^{-6} cm. The films do show enhanced p -type surface conduction.²⁸ Minimum conductivity in the bulk implies a surface conductance Δg with zero linear (or odd-order) dependence on small $\Delta W_s \equiv e\Delta V_s/kT$, where ΔV_s is the surface potential increment; the dependence is very nearly

$$\begin{aligned} \Delta g &= \frac{1}{4}\sigma_0\hat{L}_D\Delta W_s^2, \\ \hat{L}_D &\equiv [kT\epsilon/4\pi e^2(\hat{n}_0 + \hat{p}_0)]^{1/2}, \end{aligned} \quad (2)$$

where \hat{L}_D is the Debye length for change in occupation of the recombination centers. Reported conductivity σ_0 , dependence of Δg on gate charge, and field-effect mobility²⁸ are then fitted by $\Delta W_s = 1$ at zero bias, $N_s \approx 10^{14}/\text{cm}^2$ eV for surface density of electrons, and $\hat{p}_0 \approx 5 \times 10^{16}/\text{cm}^3$. This moderate \hat{p}_0 is in good agreement. Its value also indicates that the apparently thermal behavior in diodes longer than about 10^{-4} cm must result because of the fixed space charge from neutralization by the injected electrons. Large anode fields then cause pronounced heating and even avalanche breakdown.

Minimum conductivity follows from the general principle of *equality recombination*, or recombination in *equality centers* which capture electrons and holes at the same rate per unit volume.²⁹ Typical of the relaxation case, these are the donor or acceptor centers located in energy as here specified. They are realized at each of their energy levels self-consistently and by detailed

balance which depends on the scattering and the electrostatic forces. Mobile carriers are relatively few; the centers are unscreened and have extremely large capture cross sections.⁸ Only a small fraction of centers can be Coulomb attractive, and these have "space-filling" cross sections. Local space-charge neutrality at equilibrium is accordingly not maintained through the usual dielectric relaxation process dominated by Coulomb forces between mobile carriers. It is manifested through the equal capture rates instead. In the case of the alloys, there are a number of recombination centers within a mean free path, so that probability of localization and recombination after a single free path is nearly unity. The electron and hole conductivities are then equal because the carriers scatter or diffuse into (or out of) a volume element containing many atoms at the same rate.⁸ The ambipolar Hall coefficient is then negative, and the Hall-effect-Seebeck-effect anomaly may thus be simply resolved.^{8,30} Also, with the free times of carriers the same as their capture times, the equal conductivities and volume capture rates are readily seen to imply equal mean free paths and microscopic mobility ratio $\mu_n/\mu_p = (m_p/m_n)^{1/2}$, where m_n and m_p are the effective masses.

In summary, the present model for the amorphous alloys embodies new concepts of semiconductor behavior that are necessary consequences of transport and recombination fundamentals. It explains preswitching, threshold switching, and related behavior on a simple and unified electronic basis.

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