Minority-carrier injection and extraction in n -type germanium

G. Rieder,* H. K. Henisch, and S. Rahimi

Department of Physics and Materials Research Laboratory, The Pennsylvania State University, University Park, Pennsylvania 16802

J.-C. Manifacier

Centre d'Etudes d'Electronique des Sciences, Université des Sciences et Techniques du Languedoc, 34060 Montpellier, France (Received 25 June 1979)

A new injection effect predicted by a previous reexamination of the transport equations has been experimentally confirmed by probe measurements on near-intrinsic n-type germanium at low forwardcurrent densities, It implies an increase of local effective resistivity due to the difference in carrier mobility between electrons and holes. At high current densities, the familiar resistivity decrease is observed, and the changeover from one operating regime to the other occurs at current densities which are in good agreement with calculations. An analogous extraction effect for reverse currents is also documented. It leads eventually to total minority-carrier depletion within a substantial bulk region.

I. INTRODUCTION

A treatment of minority-carrier injection into semi-infinite bulk material has been given by Manifacier and Henisch' on the basis of the linearized transport equations, within the framework of ^a "small signal theory. " One of the predictions was that, in the right circumstances (injection ratio, resistivity, lifetime, etc.), minority-carrier injection could lead to an increase of local (effective) resistivity, and even to an increase of total specimen resistance. This effect would be the outcome of diffusion in any system characterized by unequal electron and hole mobilities and as long as the majority-carrier mobility is the larger. It was clear that, at higher current densities (outside the range of small signal theory), field effects would have to become more important relative to diffusion effects, and the resistance increase would be expected to disappear. The situation would then be governed by the fact that the barrier concentrations are augmented by amounts Δn and Δp , which are approximately equal in a good-lifetime semiconductor where quasineutrality prevails. That would correspond to the situation ordinarily associated with "injection, " namely a decrease of effective local resistivity and total resistance. This latter picture of the circumstances quickly became familiar after the original discovery of minority-carrier injection, so much so that the very possibility of other regimes prevailing remained totally neglected. The changeover from field enhancement (due to lowlevel injection) to field reduction (due to highlevel injection) should occur at a particular bulk field (current density) which could be estimated from simple considerations.¹ In a subsequent paper, Manifacier, Henisch, and Gasiot³ reported on computer solutions of the complete (nonlinearized) transport equations, and these showed that such a changeover was indeed predictable and in no way dependent on the approximations previously introduced. There remained, however, the need for experimental confirmation of these matters, and that has. now been provided as described below.

Figure 1 gives a schematic summary of the way in which such systems behave at different currents. In Fig. 1(a), the normalized field contours are given as a function of x' , showing the appearance of a field maximum for low currents and its gradual disappearance as the current density increases. The maximum is in fact located so close (several μ m) to the injecting interface (at $x = 0$) as to be inaccessible to experimentation by probes. x' is measured not from the injecting interface itself, but from the position of the $E=0$ point very close to it (see insert). However, for practical purposes, compared with distances which feature in probe measurements, $x' = x$.

The experiments were done in two ways. One procedure involves a simple potential-profile measurement with a single movable probe. Figure 1(b) shows a schematic potential profile for currents in the forward direction. This measurement includes the voltage drop across the barrier (located at $x = 0$) itself, which is *not* part of the present concern. However, during the analysis of bulk relationships, the intercept at $x = 0$ can be simply subtracted from each curve. The other procedure involves a pair of probes separated by a fixed small distance d , applied to the specimen at two distances x_1 and x_2 from the injecting interface. The potential difference is measured as a function of current. This is, of course, equivalent to an assessment of local average field, and the average is significant as long as d is small compared with the total extension of the distribution,

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 (c)

FIG. 1. Schematic relationship between field E, forward-current density J, voltage V, and distances x' and x . (a) As predicted by transport theory. At $x'=0$ the boundary condition is $E=0$ (see insert and text). (b) Verification procedure by one-probe measurements. (c) Verification procedure by dual-probe measurements. At the critical field E_c the (differential) sample resistivity is equal to the bulk resistivity.

and this is certainly true for the cases described. At low current densities, the local average fie1d E_1 measured for $J=J_1$ at a fixed x, close to the contact, as shown, would have to be "above normal" $(E_1>E_{\infty})$, where E_{∞} is the field in the undisturbed bulk). At a certain current density J_2 , it would be have to become normal ($E_2 = E_\infty$), and at higher current densities still, J_3 , it would be below normal $(E_3 < E_\infty)$, as traditionally associated with the injection concept. Figure $1(c)$ shows these changes in terms of the current-field characteristic for fixed x_1 and x_2 . On this characteristic there are actually two critical densities: J_2 , for which the local field becomes equal to the bulk field, and J_c , for which the conductivity dJ/dE changes from lower than bulk to higher than bulk [compare Fig. $1(a)$].

II. EXPERIMENTAL PROCEDURE

In order to observe the effects discussed above, it is desirable to have contacts with a high injection ratio. Approximate treatments of the injection ratio, $^{4-6}$ as well as experiments, 6 show that for a given barrier height the injection ratio, i.e., the fraction (of the total current) carried by minority carriers, increases with the resident (equilibrium) minority-carrier concentration (here holes). The situation is therefore favorable in nearintrinsic material. Germanium of 27.5 ohm cm resistivity and 50 μs *bulk* lifetime was chosen for this purpose. For comparison, measurements were also made on 5 ohmcm germanium of 90 μ s bulk lifetime. For that material the effects were expected to be negligible because of the low injection ratio involved. Typical crosssectional dimensions of the samples investigated were 1×1 mm, and the measured operational lifetimes varied between 10 and 20 μ s. These lifetimes were separately determined in each case by a modified Haynes-Shockley' technique, in which the contacts under investigation themselves served as emitters. The operational lifetimes are, of course, smaller than the bulk values because of the presence of surfaces. For a given lifetime, the operational lifetimes can therefore vary, depending on the surface treatment. Adjustments are possible by grinding part of the surface while leaving other parts etched.

After polishing the germanium, the samples

were etched by a solution consisting of 5 parts 48% HF, 10 parts of fuming HNO₃, 11 parts of glacial CH,COOB, and 0.1 g iodine per 100 ml, The specimens were then cleaned with trichlorethylene, boiling acetone, and deionized water. Silver contacts were thermally evaporated on one end of each sample. During the evaporation process (5×10^{-6} Torr), the temperature of the samples was held at 220'C. The other end of the sample was ground and covered with silver paste, which proved to give a low-resistance contact. As one might expect, probe measurements on etched surfaces of the samples yielded erroneous voltage profiles due to folating potentials. $8-10$ Therefore parts of the surface were ground, and

FIG. 2. Current density J versus field E. Measured with a dual-probe arrangement as displayed in Fig. 1(c). At $x=3$ mm equilibrium conditions prevail. At $x = 0.3$ mm injection effects are observed (a decrease of the differential conductivity dJ/dE near the origin and an increase with increasing E). The slope of the broken line gives the conductivity in the undisturbed bulk.

FIG. 3. Single-probe measurement [see Fig. 1(b)] of local voltage V (normalized to sample current I) versus distance x from the injecting contact.

all the measurements of potential here reported were carried out on these ground zones by currentless methods. The purpose of the grinding is to ensure that the probe contact itself in not in an environment in which electronic disequilibrium prevails. Only then can floating potentials be completely avoided. If the surface recombination is insufficient, or if only a trivial part of the surface is ground, the floating potentials come into play, leading to small discrepancies between theory and experiment close to the contact. During the measurements which produced the results presented below, such disturbing effects were altogether avoided.

III. EXPERIMENTAL RESULTS

The results presented below have been obtained on a 27.5 ohm cm n -germanium sample, with cross-sectional dimensions of 0.98×0.97 mm, length \sim 7 mm, and operational lifetime $\tau \sim$ 17 μ s. The surface on which the potential measurements were carried out was ground with polishing alumina of $3-\mu$ m grain size.

A. Forward direction

Figure 2 shows that the behavior of the 27.5 ohm cm system is indeed as predicted by Fig. 1(c). From these results the critical field E_c [see also Fig. $1(c)$, where the field current carried by ex-

FIG. 4. Comparison between calculated and measured potential contours. The broken lines show contours for $\gamma = 0.08$ and $\gamma = 1$, fitted at the origin. The insert shows the calculated field contour compared with discrete values determined from the 10- μ A contour in Fig. 3. $[\gamma_0 = \mu_p p_e/(\mu_p p_e + \mu_n n_e)$ = the current composition ratio in the undisturbed bulk.]

cess carriers and the diffusion current cancel each other, can be estimated as $E_c \approx 0.4 \text{ V/cm}$. With proper approximations one derives¹

$$
E_c = \frac{\mu_\pi/\mu_\rho - 1}{\mu_\pi/\mu_\rho + 1} \left(\frac{kT(\mu_\pi n_e + \mu_\rho p_e)}{e\tau(n_e + p_e)\mu_\pi\mu_\rho} \right)^{1/2},
$$

where μ_n and μ_p are the carrier mobilities, n_e and p_e , the equilibrium concentrations of electrons and holes, respectively, and τ the minority-carrier lifetime. For the sample used for Fig. ² $(r = 17 \mu s, n_e = 5.82 \times 10^{13} \text{ cm}^{-3}, p_e = 9.9 \times 10^{12} \text{ cm}^{-3},$ $\mu_n = 3600 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, and $\mu_p = 1800 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$), $E_c = 0.3$ V/cm, which is in fair agreement with experiment, considering the accuracy of the measurements and the approximation involved in the estimate. (Caution: In the original paper' the equation here was reproduced with a typesetting

error, corrected above.)

Figure 3 gives a set of observations at different currents, as envisaged by the schematic Fig. 1(b). At low currents the resistance increase close to the contact is quite evident; at high currents, where diffusion becomes negligible, the opposite is the case. We then observe the familiar locaI resistance decrease. The local field, for the 27.5 ohmcm specimen, is shown in the insert of Fig. 4 [corresponding to Fig. 1(a)]. (Note that the field maximum is too close to $x = 0$ to be involved by mechanical probes.) The full lines have been fitted in accordance with the Manifacier- H enisch calculations, 1 giving the injection ratios γ as the only fitting constants. The corresponding value for γ is 0.7. However, the circles in the insert of Fig. 4 represent the local slopes of the

 $10-\mu A$ line in Fig. 3, which is fitted to the experimental results. For quantitative comparisons with theory, the $V(x')$ relationship is therefore more appropriate.

As one would expect from estimated injection ratios, no resistance increase is observed for an identical contact on 5 ohm cm germanium. At high current densities, the normal resistance decrease is observed, which means that under these conditions, at any rate, the injection is not negligible, possibly due to the expected increase of γ with J.

8. Reverse direction

At $J=0$ there must, of course, be resistance continuity, which means (for the 27. 5 ohm cm sample) a resistance increase, compared with the bulk. Figure 3 also shows the situation for small reverse currents and confirms that this resistance

FIG. 5. Schematic concentration contours (quasineutrality assumed). Δn and Δp are the deviations of the electron and the hole concentrations, respectively, from their equilibrium values n_e and p_e $(n=n_e+\Delta n, p=p_e)$ $+\Delta p$).

FIG. 6. Field E versus current density J [dual-probe measurement as shown in Fig. 1(c)]. The broken lines are the slopes dJ/dE calculated for equilibrium (σ_0) and for a complete depletion of minority carriers (σ_{min}) . At $x=2$ mm (triangles) at low currents, equilibrium conditions prevail. At $x=0.3$ mm (circles) injection and extraction is observed. The resistivity increases near the origin (mentioned in the text) are not visible on this scale.

In the reverse direction, minority-carrier ex $traction^{11,12}$ leads to carrier-concentration gradients, as shown schematically (for guasineutrality) in Fig. 5. As long as the current is small, a resistance increase will again be due to differences in carrier diffusion properties. If the diffusion constants of the carriers were equal, the effects of the concentration gradients would cancel. Since electrons diffuse more quickly, their contribution dominates, in opposition to the electron field current. Thus, as in the forward direction, the situation implies an increased local field (to keep the total current constant) and hence an increase in local effective resistivity.

As the reverse current increases, concentration effects (here carrier depletion) will dominate over diffusion effects, just as they do in the forward direction. However, there is an important difference. Whereas minority-carrier injection can be increased almost indefinitely, minority-carrier extraction is limited by the number of holes which are there to be extracted. The minimum conductivity simply results as σ_{min} $=q\mu_n(n_e - p_e)$. For the Fig. 2 sample we get σ_{min} $= 28 \times 10^{-3}$ (ohm cm)⁻¹, compared with the equil- $=$ 20×10 (ominem), compared with the equi-
thrium conductivity of $\sigma_0 = 36.4 \times 10^{-3}$ (ohm cm)⁻¹. The results in Fig. 6 show that at high currents th the slope of the J vs E characteristic actually has the predicted value. As yet, field and concentration profiles for this effect have not been calculated; although the same transport equations apply,

the formulation of appropriate boundary conditions is more difficult.

IV. CONCLUSIONS

The local resistance increase described above for low currents in the forward and reverse directions arises from terms in the transport equations which are ordinarily neglected in rectification theory, and their very existence points to the need for caution in the handling of these complex relationships. In many practical situations, the current densities are often higher than those here relevant, but there are technologically important systems, e.g. , photodetectors and solar cells, in which the present considerations are likely to have an appreciable influence on the internal resistance and hence the efficiency. The precise effect of light on these relationships remains to be systematically explored. An analogous extraction effect is here documented, as far as is known, for the first time. It saturates with the total depletion of minority carriers, extending over substantial distances (e.g., > 1 mm for sufficiently high currents) into the bulk material.

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- *On leave of absence from the Institut fur Hochfrequenztechnik der Technischen Universität Wien, A-1040 Vienna, Austria.
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