the resolution of the structure and provide the basis for a theoretical evaluation of the effective mass of holes. The degeneracies that have been observed in the Si(Al) data appear to be consistent with present knowledge of the structure of the valence bands in Si.

In general, it is advantageous to select impurities which have the smallest ionization energies in order to enhance the probability of transitions from the ground state to the excited states as well as to the bound Landau levels in the continuum. This can be understood in terms of the overlapping of the wave functions for the states involved in the transition. The wave functions of the excited states are relatively independent of the depth of the ground state, but the ground-state wave function is strongly influenced by the Coulomb center. Experimentally, the absorption lines in the photoexcitation spectrum of shallow impurities will be relatively much more intense and their resolution will be improved. However, of the principal monovalent donors and acceptors in silicon, only the donor bismuth and the acceptor aluminum, which are not the shallowest, have excited states whose excitation spectrum occurs in the spectral region of maximum dispersion for a KBr prism. The choice of KBr prism dispersion combines the benefits of a spectral region for which a moderate source intensity is available and also one that is relatively free of atmospheric and silicon lattice absorptions. Furthermore, the benefits obtained in measuring spectra with the usual silver chloride sheet polarizer are limited to the region below 25 microns by the cutoff of that material. If one were to accept the experimental disadvantages of the longer wavelength region, then similar measurements of the shallower impurities, boron and antimony, would probably show the transitions to the bound Landau levels, which would reveal the effective mass of the carrier and the ionization energy of the impurity. Such results have been obtained in Ge for shallow impurities in the far infrared spectral region.[4,5,10]

It may be concluded from these observations of the Zeeman effect of excited impurity states in a semiconductor that the method provides a capability of making infrared measurements of heavy effective masses with the use of moderately high magnetic field intensities. Electron effective masses as large as m_0 could be measured with a field of 80 kgauss.

VI. ACKNOWLEDGMENTS

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Rectification without Injection at Metal-to-Semiconductor Contacts

N. J. HARRICK
Philips Laboratories, Irvington-on-Hudson, New York
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A recent publication shows that extraction in the semiconductor bulk may occur for either direction of current flow through the same metal-to-semiconductor contact when an insulating layer separates the metal and the semiconductor and the field effect determines the surface barrier under the metal. It is shown here that strong rectification, whose direction depends only on the bulk type, may occur for such contacts to extrinsic, but not intrinsic, semiconductors. Thus, rectification, without injection, may occur at the metal-to-semiconductor contact for the two-carrier system.

EXTRACTION in the semiconductor bulk can occur for either direction of current flow through the same metal-to-semiconductor contact if the field effect determines the surface barrier under the metal.[1,2] The field effect can predominate in this way when an oxide or other high resistance layer separates the metal and the semiconductor surface. It is the purpose of this paper to point out that strong rectification without injection[3] may occur for such contacts to extrinsic, but not intrinsic, semiconductors. This point and its implications for other semiconductors was not appreciated in an earlier discussion of this extraction phenomenon.[1]

Evidence for this phenomenon is shown in Fig. 1, which gives the J-V and J-Δp characteristics for two such metal-to-semiconductor contacts. Here the p-type bulk exhibited surface layers which were initially p^+, although similar curves were observed for this sample with n-type and neutral surfaces. Extraction is observed for negative currents (metal negative) with no saturation in the J-V characteristic. This is expected as the

[1] N. J. Harrick, Phys. Rev. **115**, 876 (1959).
[2] N. J. Harrick, Phys. Rev. Letters **2**, 199 (1959).
[3] The rectification mechanism described here is to be distinguished from the earlier rectification theories (i.e., diode and diffusion) which considered a one-carrier model and did not involve injection or extraction.

applied voltage makes the surface more strongly p type and the current can increase indefinitely for extraction (field aided)[4] for the p^+-p type of structure. For positive currents (metal positive), injection (field opposed) is observed at first and extraction (field opposed)[4] at higher currents accompanied by an abrupt increase in resistance to the current. This change-of-contact characteristic can be understood if the applied voltage reduces the height of the p-type barrier and actually reverses it at higher currents, resulting in an n-p type of structure.[5] This n-p structure is biased in the reverse direction and is known to saturate in current. If no initial barrier is present, n- and p-type layers are immediately established for positive and negative currents, respectively. Any accumulation layer serves only to shift the turnover point in the J-V characteristic. The direction of rectification of the type under discussion depends only on the bulk type.

That rectification of the type under discussion will occur can be seen from an examination of the current-voltage equations. The extraction currents (V is negative) for p^+-p and n-p structures with high barriers and neglecting surface generation are given, respectively, by[6]

$$J_{\mathrm{FA}}\left[\left(\frac{\sigma_h}{\sigma}\right)_p-\left(\frac{\sigma_h}{\sigma}\right)_{p^+}\right]=\frac{qD_p}{L_{\mathrm{FA}}}p_{\mathrm{op}}(e^{qV/kT}-1),$$

and

$$J_{\mathrm{FO}}\left[\left(\frac{\sigma_h}{\sigma}\right)_p-\left(\frac{\sigma_h}{\sigma}\right)_n\right]=\frac{qD_p}{L_{\mathrm{FO}}}n_{\mathrm{op}}(e^{qV/kT}-1).$$

The deficit carrier distributions for extraction are field aided (FA) and field opposed (FO) for the p^+-p and n-p structures, respectively. p_{op} and n_{op} are the equilibrium hole and electron densities, respectively, in the p-type bulk. The terms σ and σ_h refer to the total and hole conductivities, respectively, in the p-type bulk and n- or p^+-type surface, according to the subscripts. The L's are the drift-diffusion lengths in the p-type bulk with limiting values of $\mu^*E\tau$ and D/μ^*E for the field-aided and field-opposed distributions, respectively. The voltage in these equations refers to that just across the junction. J_{FO} saturates, as the voltage increases, in the manner expected for a reverse biased n-p junction. J_{FA}, however, cannot saturate because the conductivity term tends towards zero, i.e., $(\sigma_h/\sigma)_p=(\sigma_h/\sigma)_{p^+}$, as the condition of complete extraction is approached. One must be careful in comparing the two current equations because a high voltage cannot easily be developed across the p^+-p type of junction. This is so because a hole density about the same as that found in the p-type bulk is also found in the space charge region and the junction thus is "shorted out by the valence band," hence, the current is limited by the resistance of the bulk. Mathematically, the equation does not hold for a large voltage applied across the junction voltage because extraction violating the assumption of charge neutrality would then occur. The two current equations are identical for intrinsic bulk, hence no rectification of the type under discussion can occur. Such contacts make good collectors but will not work as emitters for transistors.

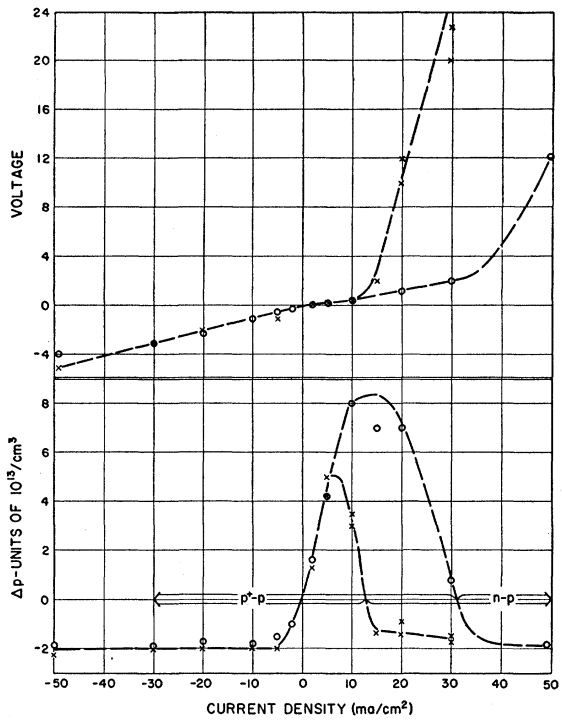

FIG. 1. Current versus added carrier density and current-voltage characteristics of two contacts exhibiting the phenomenon extraction for either direction of current flow for near-intrinsic, p-type germanium with a p^+ surface. The voltage measured includes that across one-half centimeter of bulk. The sign of the current and voltage refers to the polarity of the metal with respect to the semiconductor.

The rectification mechanism outlined here can be positively identified for near intrinsic materials where extraction can easily be observed as is done for the two cases shown in Fig. 1 and with the aid of photovoltage measurements.[1]

Rectification observations by Hartmann[7] can be explained by the mechanism outlined here. He placed shellac of about 10^{-4} cm thickness between copper and cuprous oxide (p type) and zinc oxide (n type) semiconductors and found rectification in opposite directions and of sign consistent with the predictions of the present mechanism.

[4] Field-aided and field-opposed terms as they apply to injection and extraction are defined by N. J. Harrick [J. Appl. Phys. **29**, 764 (1958)].

[5] Such reversals in J-Δp characteristics have definitely been related to reversals in barrier type under the contact with the aid of photovoltage measurements (see reference 1).

[6] These equations arise from applying a p-n junctionlike theory to the metal-to-semiconductor contact and resemble those described in reference 4 for the p-n junction. The experimental and theoretical foundations underlying the application of these equations to the metal-to-semiconductor contact will be discussed in a forthcoming publication.

[7] W. Hartmann, Physik Z. **37**, 862 (1936).