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Significance of Composition of Contact Point in Rectifying Junctions on Germanium

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INTERPRETATIONS of the relevance of the composition of the metal point to the properties of point-contact rectifiers have been modified in recent years. Until fairly recently, properties of germanium- and silicon-rectifiers were felt to be directly related to the work function of the metal point.¹ However, the failure of several experimenters to confirm the predictions of this theory led Bardeen² to propose that localized states, having energies in the "forbidden" range between the filled and conduction bands, may exist at the surface of the semiconductor. Such surface states produce at the surface of the semiconductor a barrier whose properties depend on the density and distribution in energy of the surface states. For a high density of surface states, this theory indicates that the rectification properties of a metal-semiconductor junction will be independent of the metal.

However, experiments with *n*- and *p*-germanium transistors indicate that the composition of the contact point *can* influence the properties of rectifying junctions. While such results are not inconsistent with Bardeen's theory, they do indicate that surface states can be considerably modified in particular junctions. Briefly, the significant feature of the metal point is its content of donors and acceptors. By means of an electrical treatment known as forming, it appears that donors or acceptors from the point can be introduced to or into the germanium, thereby affecting the space-charge region and the electrical properties of the junction. Two illustrations of the role of point composition in determining the properties of metal-germanium junctions are given below.

(1) It is observed that a pressure contact made with any metallic point to *p*-germanium usually results in but poor rectification. This has been ascribed to the existence of surface states which are such that the potential barrier they produce is of negligible height.³ For many common contact materials, electrical forming of such a junction does not markedly improve the rectification. However, for a point which contains donors, such as

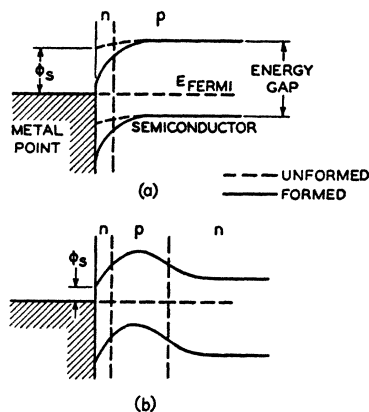


FIG. 1. Energy level diagrams showing rectifying barriers at contacts containing donors: (a) *p*-germanium; (b) *n*-germanium.

TABLE I. Forward and reverse currents at 1 volt of rectifying junctions on *n*-germanium as functions of antimony concentration in the metallic electrode.

Row	Wgt. % Sb	I_F (ma)	I_R (ma)
A	None	35	0.035
B	0.0001	33	0.026
C	0.001	37	0.10
D	0.01	3.1	2.4

phosphor bronze, it is found that forming increases the forward conductivity of the rectifying junction, thereby improving it as a rectifier and as an emitter of electrons in the *p*-germanium transistor.⁴ The changes which are observed on forming with a phosphor bronze point can be interpreted as the result of the introduction of donors from the point to the germanium, with a resultant lowering of ϕ_s , the effective work function for electrons leaving the metal, as shown in Fig. 1a.

(2) In a recent letter Shockley⁵ discusses theories of α , the current-multiplying factor in the transistor. According to one of these, the *pn*-hook theory, the space-charge region about the collector junction of an *n*-germanium transistor is as shown qualitatively in Fig. 1b. Results of experiments with contact-point alloys are consistent with Shockley's model and appear to indicate that the *n*-zone can be produced by electrical forming if donors are present in the point-electrode.⁶ *n*-germanium transistors were prepared having as collectors a series of alloys graded with respect to donor (Sb) concentration. After forming the collectors (using the same emitter composition in all transistors), it was found that α increased with antimony concentration and that the forward and reverse current of the collector junctions were as shown in Table I.

Mean values are given for groups of 4 or 5 junctions. The data may be interpreted as follows:

The values of rows A and B represent fairly good rectifying junctions in *n*-germanium; ϕ_s is high and the reverse current of electrons is small. Since ϕ_s is high, a *p*-type inversion layer exists and a large hole current is present in the forward direction. Row C: the forward current is still large, but the reverse current has increased. The increase in antimony concentration has caused some lowering of ϕ_s , possibly only at small patches in the contact interface. Row D: sufficient antimony is present to produce an *n*-type inversion layer, as in Fig. 1b, which completely encloses the metal point. ϕ_s is here quite low and as a result the reverse current of electrons is large and the forward current of holes is small.

While the examples given here pertain to donors in the point electrode, it appears that corresponding effects can be caused by acceptors.

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⁶ We discuss here only the *n*-zone. Experimental results which indicate the existence of a chemical *p*-zone have been described by L. B. Valdes, to be published in *Proc. Inst. Radio Engrs.*

Microwave Study of Ge, Si, and S Masses*

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THE relative masses of the stable Ge isotopes of even mass number and the mass difference ratios ($S^{33}-S^{32}$)/($S^{34}-S^{32}$) and ($Si^{30}-Si^{29}$)/($Si^{30}-Si^{28}$) have been determined from the isotopic shift in the pure rotational absorption spectrum of GeH_3Cl^{85} , $O^{16}C^{12}S$, and SiH_3Cl^{85} , respectively.