University of California in supplying the exit strips used in this research is gratefully acknowledged. The work was supported in part by a grant from the Research Institute of the University of Texas.

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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 Bardeen[2] 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 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.

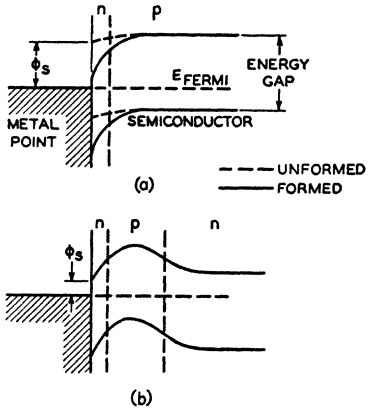

FIG. 1. Energy level diagrams showing rectifying barriers at contacts containing donors: (a) *p*-germanium; (b) *n*-germanium.

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

(2) In a recent letter Shockley[5] 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.

The writer is indebted to Mr. R. J. Kircher for contributions to the experimental data on point compositions.

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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^{35}, $O^{16}C^{12}S$, and SiH_3Cl^{35}, respectively.

TABLE I. Experimentally determined masses of the even Ge isotopes compared with masses calculated from semi-theoretical mass formula, assuming exact agreement for Ge^{70} and Ge^{74}.

Nucleus	Experimentally determined masses	Masses calculated from Bohr-Wheeler formula
Ge^{70}	69.94952	69.94952
Ge^{72}	71.94848	71.94816
Ge^{74}	73.94862	73.94862
Ge^{76}	75.94994	75.95077

Assuming the Ge^{70} and Ge^{74} masses to be correctly given by the Bohr-Wheeler formula, the Ge^{72} and Ge^{76} masses were calculated in a manner analogous to that used in determining the relative masses of Se from the OCSe spectrum.[1]

The experimentally determined masses and the values given by the semi-empirical mass formula[2] are listed in Table I. The error in mass determination due to a combination of experimental error and uncertainty due to zero-point vibration, is 0.4 mMU. These results, plotted in Fig. 1, indicate essential agreement with the semi-empirical mass formula although the Ge^{76} mass is 0.8 mMU less than predicted and must be regarded as a real deviation. It would appear that the curvature of the mass defect *vs* mass number curve is slightly smaller than predicted, similar to the findings[1] for Se.

Of particular interest is the mass of Ge^{72}, which has 40 neutrons. According to the assignment of energy levels in the nuclear shell model by Mayer,[3] and Haxel, Jensen, and Suess,[4] 40 neutrons should complete a $p_{1/2}$ subshell, so that a small break might be expected in the mass defect curve at Ge^{72}. As pointed out elsewhere,[1] this break should be unaffected by errors in the assumed Ge^{70} and Ge^{74} masses or by uncertainties due to zero-point vibrations. That no such break occurs is interpreted to mean that the $p_{1/2}$ and $g_{9/2}$ levels lie within 0.3 mMU, for any larger separation would give an unambiguous break in the mass defect curve.

From the absolute frequencies of the $J=1\rightarrow2$ transition in $O^{16}C^{12}S$, corresponding to S^{32}, S^{33}, and S^{34}, which were measured to an accuracy of 5 kc or better, and from the absolute frequencies of the $J=1\rightarrow2$ transition in SiH_3Cl^{35} for the three stable isotopes of Si, which were measured to an accuracy of 15 kc, the mass difference ratios $(S^{33}-S^{32})/(S^{34}-S^{32})$ and $(Si^{30}-Si^{29})/(Si^{30}-Si^{28})$ were calculated, neglecting zero-point vibrations, and were found to be

$$(S^{33}-S^{32})/(S^{34}-S^{32})=0.500714\pm0.00003;$$
$$(Si^{30}-Si^{29})/(Si^{30}-Si^{28})=0.49941\pm0.00005.$$

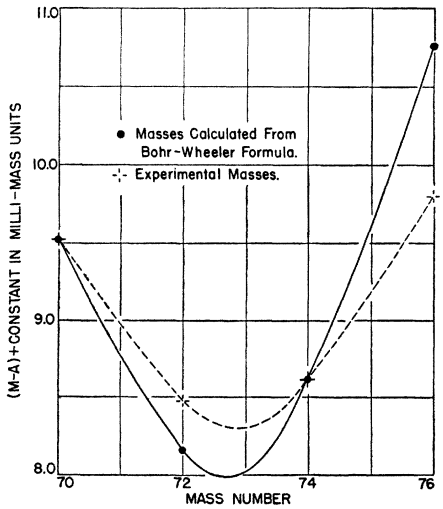

FIG. 1. Variation of masses of even Ge isotopes as a function of mass number.

TABLE II. Experimentally determined sulfur masses.

$S^{32}=31.98199\pm0.00021$	$S^{35}=34.98046\pm0.00035$
$S^{33}=32.98187\pm0.00025$	$S^{36}=35.97954\pm0.0006$
$S^{34}=33.97890\pm0.0003$	

The sulfur mass differences were measured by Davisson[5] using nuclear reactions, and he obtained $(S^{33}-S^{32})/(S^{34}-S^{32})=0.50060\pm0.00008$. From mass spectrometer experiments, Duckworth, Preston, and Woodcock[6,7] obtain for the silicon masses

$$(Si^{30}-Si^{29})/(Si^{30}-Si^{32})=0.499341\pm0.00006.$$

The agreement between the two sets of results justifies an earlier estimate[1] of the outside limit of the error introduced by neglecting zero-point vibrations.

The $O^{16}C^{12}S^{36}-O^{16}C^{12}S^{34}$ separation was measured by Low and Townes;[8] and Koski, Wentink, and Cohen[9] measured the $O^{16}C^{12}S^{35}-O^{16}C^{12}S^{34}$ separation. Combining these results with ours, the sulfur masses were determined using S^{32} and S^{34} as

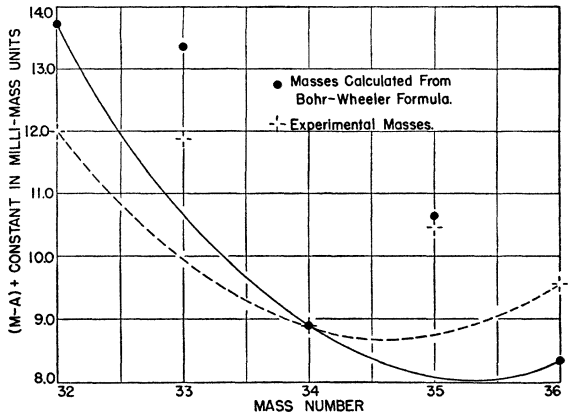

FIG. 2. Variation of sulfur masses as a function of mass number. The masses given by the Bohr-Wheeler formula have been adjusted so that the predicted S^{34} mass coincides with the experimental value.

reference masses and taking[10] $S^{32}=31.98199$, and $S^{34}=33.97890$, using the $(S^{34}-S^{32})$ difference measured by Davisson.[5] The sulfur masses, listed in Table II and plotted in Fig. 2, give for the odd-even mass differences in S^{33} and S^{35}, 2.0 ± 0.3 and 1.7 ± 0.3 mMU, respectively, compared with $\delta=0.036/A^{3/4}=2.6$ and 2.4 mMU, respectively, given by the Fermi formula.

The error stated is a combination of experimental error and the margin of error to be allowed in fitting a curve to the experimental points. In this low mass number region the semi-empirical mass formula deviates from the experimental mass by as much as 3 mMU, and so for a comparison with the experimental masses it has been adjusted to the S^{34} mass. The measured frequencies and other details will appear in a forthcoming publication.

The authors wish to express their indebtedness to Professor Townes for suggesting this problem and for his continual aid and interest.

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