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Secondary Electron Emission from Germanium

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Secondary emission by electron bombardment has been measured for single crystals of Ge with *p-n* junctions. Maximum yield was found in the range $\delta=1.15\pm0.03$, at $V_p\approx500$ volts and room temperature. Increasing temperature decreased the yield because of a small interaction between the internal secondaries and the lattice. The most probable energy of emission was 1–2 ev. There was no change in yield with donor or acceptor concentration up to $10^{19}/cm^3$, and in particular there was no detectable effect of the space-charge fields under the surface. These results form the basis for discussion of the secondary emission process in semiconductors as compared with metals and insulators.

INTRODUCTION

THE secondary electron emission properties of metals are fairly well established and progress is being made in the study of insulators.[1,2] However, relatively few studies have been made of those intermediate materials, the semiconductors. The aims of the present study are: (1) To measure carefully the significant secondary emission properties of a semiconductor and to interpret those properties in terms of current theory. (2) To investigate the effect of subsurface electric fields under controlled conditions. This is relevant to the process of field-enhanced emission from insulators.

Germanium was chosen as the target material because so much is now known of its electrical properties[3] and because it is available in single crystals of great purity.

METHOD AND APPARATUS

A method of measurement previously used for insulators was employed.[4,5] The target of Ge is centered in a hemispherical collector electrode. A pulsed electron beam of energy V_p strikes the target and the secondary current flows to the collector. Current in the target circuit is amplified and displayed on an oscilloscope, showing the primary current when the collector is negative, and the excess of secondary over primary when it is positive.

TABLE I. Composition of Ge wafers.

Wafer	A	B	C,D
ρ_n (ohm cm)	0.06	5.5	0.0046
Additive	Sb	As	Ga+Sb
N_n (cm^{-3})	6×10^{16}	6×10^{14}	3.4×10^{18}
ρ_p (ohm cm)	0.08	0.8	0.008
Additive	Sb+Ga	As+Ga	Ga
N_p (cm^{-3})	8×10^{16}	7×10^{15}	1.4×10^{19}

The wafers forming the targets were cut from single crystals of Ge grown by drawing from the melt, with carefully controlled impurity additions.[6] Four wafers were used, called here A, B, C, and D. The first three, used in secondary emission measurements, were about 5×7 mm on the side and 2 mm thick. The fourth, D, was a little larger and was used for the contact potential work. D was cut from the same large single crystal as C where they faced each other across the saw cut. They should, therefore, present closely the same properties. The crystals were grown so as to be p type at one end and n type at the other, with a sharp p-n junction between. From these the wafers were cut so as to have the junction perpendicular to the side and bisecting the longer dimension. In wafers A and B the face was cut parallel to the (100) plane, and in C and D parallel to the (111) plane. The properties of the wafers are given in Table I, the resistivity ρ of the p-type and n-type portions being measured and the excess density of donors N_n and acceptors N_p calculated from these values.[7]

The surface of the wafers was first finely abraded, then etched with a mixture of HNO_3, HF, and Br and finally washed carefully with distilled water leaving the surface unpolluted.

The targets were mounted in experimental tubes with great cleanliness. These were pumped on a system with mercury vapor pumps, with extensive outgassing. The usual procedure was baking of the tubes for hours at 400–500°C, heating the wafers to a dull red temperature, and sealing off at a pressure near 10^{-8} mm Hg. Some wafers were resurfaced and repumped several times.

EXPERIMENTAL RESULTS

A. δ-V_p Curves

The yield δ as a function of the primary energy V_p is plotted in Fig. 1 for the case of wafer C. Curve a refers to room temperature. The maximum yield is about 1.2, at about 500 volts. The other wafers gave values very close to this, the range for different wafers with repeated treatments being $\delta_{max}=1.12-1.18$. This

* Now with Edison Laboratory, Thomas A. Edison, Inc., West Orange, New Jersey.
[1] K. G. McKay, "Secondary electron emission," *Recent Advances in Electronics* (Academic Press, Inc., New York, 1948), Vol. 1, p. 65.
[2] A. J. Decker and A. van der Ziel, Phys. Rev. **86**, 755 (1952).
[3] E. M. Conwell, Proc. Inst. Radio Engrs. **40**, 1327 (1952).
[4] J. B. Johnson, Phys. Rev. **73**, 1058 (1948).
[5] J. B. Johnson and K. G. McKay, Phys. Rev. **91**, 582 (1953).
[6] They were grown by G. K. Teal and M. Sparks.
[7] Pearson, Struthers, and Theuerer, Phys. Rev. **77**, 809 (1950).

is within 5 percent of the value given by Koller and Burgess[8] for a target of unspecified composition and treatment.

We can conclude with some assurance that the secondary yield of Ge within the range of impurity content used here is essentially unchanged by the donor or acceptor additives. A foreign atom concentration to the extent of 0.01 percent does not alter the secondary emission process, which is still characteristic of the Ge lattice. These foreign atoms evidently do not act as "emission centers." Being ionized they might not be expected to, so that such centers could still occur under other circumstances.

B. δ *vs* Temperature

No appreciable temperature variation of yield has been found in the case of clean metals.[9] Insulators are found to have a marked reduction of yield with increasing temperature.[5,10] Curve *b* of Fig. 1 shows an appreciable reduction of yield in Ge in the range of V_p near and above the maximum. The variation over a range of

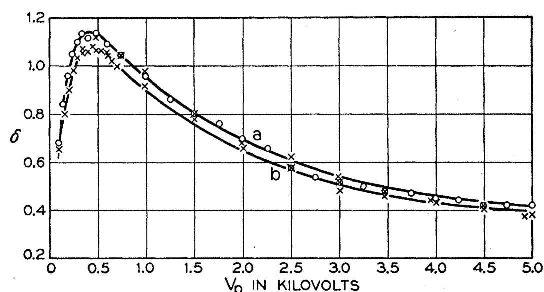

FIG. 1. Yield δ *vs* bombarding voltage V_p for wafer *C*. Curve (*a*) room temperature, (*b*) $T=525°C$.

temperatures is shown in Fig. 2 measured near the second crossover where $\delta=1.00$ and with a thermocouple on the target. As with insulators, the reduction in yield is not merely proportional to the yield itself but also depends on V_p, being smallest for low V_p. This indicates that the effect is not due to increase of work function with temperature but is concerned with the body properties.

It could be argued that the decrease in yield at higher temperatures is caused by the increased interaction between the internal secondaries and the augmented density of free electrons in the conduction band. This argument can be eliminated as follows: At room temperature, there is no appreciable difference between the yield of target *B* and target *C* although *B* contains

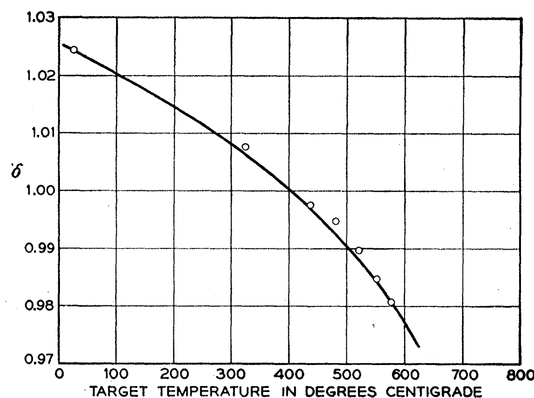

FIG. 2. Yield δ *vs* target temperature. $V_p=800$ volts.

6×10^{14} free electrons/cm^3 on the *n* side and *C* contains, 3.4×10^{18} electrons/cm^3. At 600°C, the respective free-electron concentrations have risen to 7×10^{16}/cm^3 and 3.5×10^{18}/cm^3. However, in both cases the high-temperature yield has dropped below the room temperature yield by the same amount in spite of the disparity in the proportional increases in free-electron concentration. From this we must conclude that the effect on the yield of a free-electron concentration of up to 3×10^{18}/cm^3 is negligible.

Another conceivable mechanism for the temperature coefficient of δ is that the range of the primaries increases with temperature. This appears entirely unreasonable. Thus we conclude that in Ge collisions of electrons with the lattice are a small but appreciable source of energy loss of the internal secondaries, the loss to free electrons being negligible and that connected with raising electrons across the forbidden gap of 0.7 ev predominating. This distinguishes the semiconductor from the metal where the predominant loss is to nearly free electrons with negligible temperature effect, and from the insulator where, at energies that are low but still sufficient for escape the loss in lattice collisions must predominate and the temperature effect is therefore relatively large.

C. Energy Distribution

By applying retarding or aiding potentials to the collector, the distribution-in-energy of the secondary electrons was estimated. Figure 3 shows the current in the target circuit as a function of potential on the collector, obtained with wafer *B*. The corresponding distribution in energy obtained by differentiation is given in Fig. 4. The contact potential of the collector, a film of colloidal graphite, should not be far from that of the Ge target[11] so that the curve needs little shift because of contact potential. This would make the most probable energy of the secondaries about 1 ev. However, the flat target violates the condition for the

[8] L. R. Koller and J. S. Burgess, Phys. Rev. **70**, 571 (1948).

Note added in proof:—A paper by H. Gobrecht and F. Speer [Z. Physik **135**, 602 (1953)] reports values of δ for targets of polycrystalline and evaporated germanium generally somewhat higher than ours and showing a slight rise at greater impurity content than we used here.

[9] D. E. Wooldridge, Phys. Rev. **58**, 316 (1940).

[10] J. B. Johnson, Phys. Rev. **92**, 843 (1953).

[11] The work function of evaporated films of Ge is about 4.8 volts according to Apker, Taft, and Dickey, Phys. Rev. **74**, 1462 (1948).

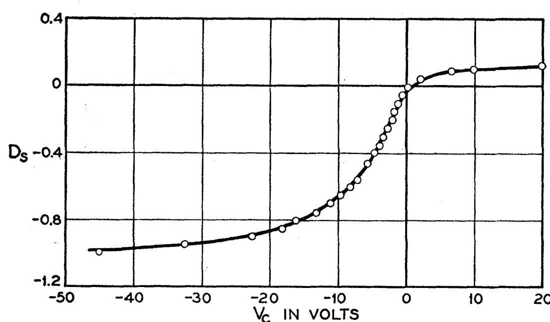

FIG. 3. Retarding potential curve for wafer B. D_s is proportional to $i_s - i_p$. $V_p = 500$ volts.

true spherical symmetry required, and also, there is the condition of "negative energy" electrons on the right that usually appear in this type of measurement. These may be due to tertiary electrons released from the collector by reflected primaries, or to patch potentials on the surface of the target that require the collector to be positive in order to overcome their retarding effect on secondaries from certain areas. In any case, the result is such that this kind of distribution curve should not be taken too literally because the maximum may be shifted by these extraneous effects.

D. Yield *vs* Sub-Surface Electric Field

One of the mechanisms invoked in the process of secondary electron emission from insulators is field-enhancement. This means that an electric field existing within the target near the bombarded surface may increase or decrease the yield of secondary electrons. Since sub-surface fields are known to exist in Ge, with calculable strength and distribution, the opportunity is presented of quantitatively observing the effects of such fields.

The energy levels available to mobile electrons and positive holes in Ge do not remain at a constant distance from the Fermi level as the surface is approached. This is attributed to the presence of surface states where holes or electrons are trapped, leaving a space-charge layer under the surface to balance the surface charge, the layer being largely devoid of the mobile carriers. Thus, in this layer there is an electric field that can be calculated on plausible assumptions, and the field in p-type Ge is opposite in direction from that in n-type Ge. No difference greater than 0.1 volt in external contact potential has been found[12] between p-type and n-type Ge treated the same way, and therefore, the fields must exist inside rather than outside the surfaces. It was this fact of having opposite fields on the two sides of a sharp p-n junction with the surfaces subjected to exactly the same treatment that made this experiment on secondary yield attractive.

Target C was particularly well adapted for this comparison, since in it the high carrier concentration makes the thickness of the space-charge layers comparable with the range of the electrons involved. Calculations[13] show that in this specimen the bottom of the conduction band is lowered in energy by 0.30 volt on the n-type side, and the top of the valence band is raised by 0.35 volt on the p-type side, relative to the Fermi level. We do not know the exact distribution of this total shift of 0.65 volt, but a serviceable assumption is that it is divided equally between the two space-charge layers at the n and the p surfaces, $\Delta V = 0.32$ volt each. By the procedure used for calculations on the Schottky depletion layer, we can compute the thickness of this layer, assuming that the impurity concentration remains the same from the interior to the surface,

$$l_0 = (K\Delta V/2\pi eN)^{\frac{1}{2}}. \tag{1}$$

N is the density of donors or acceptors, K the dielectric constant which is here 16, e the electronic charge. We obtain for the n-type side $l_{0n} = 130$A and for the p-type side, $l_{0p} = 65$A. The corresponding fields at the surface are $E_0 = 2\Delta V/l_0 = 0.49\times 10^6$ and 0.98×10^6 v/cm. The potential drop with respect to the surface at the depth X is given by

$$\Delta V_X = E_0 X[1-(X/2l_0)]. \tag{2}$$

In the other specimens with lower values of N, the l_0 is much greater, the effective potential difference somewhat less, and the fields smaller.

The surface field can act most effectively on the internal secondaries if the depth of origin of the secondaries is nearly the same as the thickness of the space-charge layer. Diemer and Jonker[14] have presented reasons for believing that in nickel the range of 500-volt primary electrons is 50A. On the basis of the ratio of densities, this should be about 85A for Ge, both materials having $V_{p\max}$ at about 500 volts. Similarly, Bruining[15] deduces that the mean depth of origin of

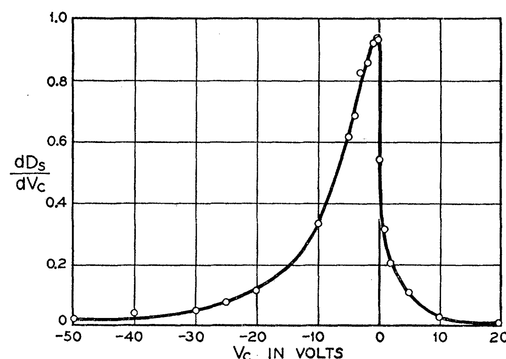

FIG. 4. Approximate energy distribution of secondary electrons obtained by differentiation of the curve in Fig. 3.

[12] W. H. Brattain and J. Bardeen, Bell System Tech. J. **32**, 1 (1953).

[13] W. Shockley, *Electrons and Holes in Semiconductors* (D. van Nostrand and Company, Inc., New York, 1950), Chap. 10.

[14] M. Diemer and J. L. H. Jonker, Philips Research Repts. **5**, 161 (1950).

[15] H. Bruining, *Die Sekundär-Elektronen-Emission fester Körper* (J. Springer, Berlin, 1942), p. 71.

secondaries from 500-volt primaries in nickel is 30A, or 50A in Ge if the density relation holds. These values are of the same order of magnitude as the calculated thickness of the space-charge layer for wafer *C*, so that in this specimen the effect of the internal field should be nearly a maximum.

The internal fields are in such directions as to urge electrons toward the surface in the *p*-type material and toward the interior in the *n* type. The potential change between the surface and the point of origin of a carrier may be considered for that carrier to be equivalent to a nearly comparable change in the work function at the surfaces. This should have an effect on the secondary yield, which can roughly be computed by a relation derived by Wooldridge[16] for metals of high work function, and which agrees well with data by Treloar[17] on molybdenum and tungsten. It is

$$\Delta \log_e \delta_{\max} \doteq 0.1 \Delta\varphi, \qquad (3)$$

where $\Delta\varphi$ is the change in work function. By relation (2) the potential drop ΔV_X at 50A is for the *n*-type side 0.20 volt and for the *p*-type side 0.30 volt. If we identify the sum of these with a change in work function, $\Delta\varphi = 0.50$ volt, then by relation (3) $\delta_{\max}$ should change by 5 percent in going from one surface to the other across the junction.

Accordingly, numerous point-by-point scans were made with a sharply focused primary beam over the surfaces and across the junction. Figure 5 reproduces one of these scans on wafer *C*. The value of δ is plotted against the beam position control reading, at a value of V_p where $\delta \doteq 1.00$. The scan covers about $\frac{1}{4}$ in. on the wafer, and the junction is near the middle of the scan from left to right. Small variations in δ were found along the surface, but in the many runs made on this and the other wafers there was never any step as large as 1 percent that could be identified with the junction.

Explanations for this absence of field effect can be postulated as follows:

(a) In spite of evidence at lower impurity concentration there may be in this heavily doped specimen *C* an external difference of contact potential that reduces the internal potential drops.

(b) In the heat and vacuum treatment of the wafers,

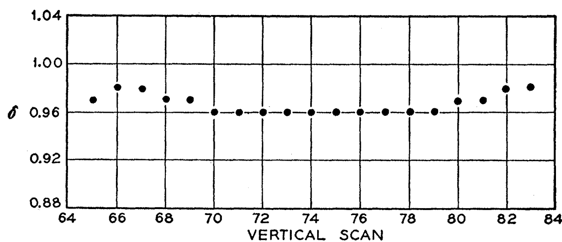

FIG. 5. Yield δ *vs* spot position on wafer *C*. $V_p = 1000$ volts. The *n*-*p* junction cuts across the middle of the scan.

[16] D. E. Wooldridge, Phys. Rev. **56**, 562 (1939).
[17] L. R. G. Treloar, Proc. Phys. Soc. (London) **49**, 392 (1937).

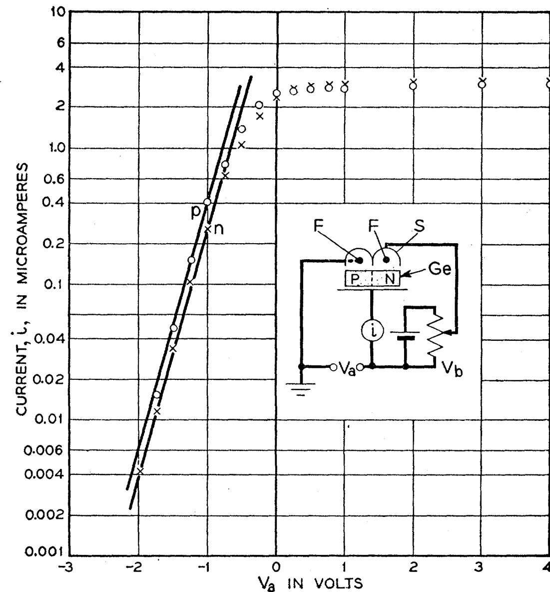

FIG. 6. Measurement of contact potential difference between *n*- and *p*-type sections of wafer *D*.

the second additive may have evaporated preferentially from the surface, leaving both surfaces either *n* or *p* type to a depth as great as the maximum escape range of the secondaries.

(c) There is a subsurface field, but the collision processes of the secondaries are such that momentum in the direction of the surface gained by the electrons from the field does not build up but is dissipated at each inelastic collision.

Hypothesis (a) was checked on wafer *D*, with measurement of contact potential difference (cpd) between the two sides of the junction. Contact potential measurements were made with the use of a tungsten filament as electron emitter and the Ge as counter electrode. The usual semilog plots of current *vs* voltage established the difference in contact potential between different areas of the Ge. The measurements were made with a circuit in which the filament heating current was zero in the alternate ac half-cycles where the current readings were observed. This was done after various vacuum treatments, from long bake at up to 600°C to short bake at 300°C. In no case was the cpd more than about 0.2 volt. Figure 6 gives the result for the case of the mildest vacuum treatment where there could have been no appreciable evaporation of any constituent. The difference between the two retarding-potential curves is within 0.1 volt. Confirming other result, then, there is no appreciable difference in cpd between the *n*- and *p*-type sides of this specimen.

Hypothesis (b) was checked with wafer *C*. After a fresh etch it was mounted in the tube which was then processed by long pumping and by outgassing the electron gun but without heating the wafer above room temperature. The wafer was then scanned in the usual

way. The δ_{max} was higher than normal, about 1.6, presumably because of surface contamination, since there was no detectable change in $V_{p\max}$. There was still no step at the junction. Evaporation of a constituent could not have been a factor in this test.

If indeed, then, the space-charge layer exists as calculated and there is no change in material constituents to within very close to the surface, hypothesis *c* remains. It does not seem plausible if the internal secondaries lose energy in steps at each collision that are nearly independent of their energy. If, on the other hand, the energy lost at a collision is proportional to the energy of the colliding electron, then these results would probably ensue.

CONCLUSIONS

1. The yield from Ge is independent of normal donor or acceptor additives and is, therefore, determined by the intrinsic properties of the Ge lattice.

2. The yield from Ge has a small but appreciable temperature coefficient. This is taken as evidence for a small interaction between the internal secondaries and the lattice.

3. The interaction is negligible between internal secondaries and free electrons or positive holes up to concentrations of about $10^{19}/cm^3$.

4. No evidence has been found that strong subsurface fields affect the yield from Ge. It is believed that this is a result of the detailed mechanism of energy loss of the internal secondaries and that it does not rule out the possibility of field effects in other materials such as insulators.

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Phase Transitions in Ferroelectric $KNbO_3$†

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It is shown that ferroelectric $KNbO_3$ undergoes another phase transition at $-10°C$ in addition to two phase transitions previously reported at 225° and 435°C. At this lowest phase transition $KNbO_3$, on cooling, changes its orthorhombic structure to a rhombohedral one, and this change is accompanied by a sharp change of the dielectric constant. The specific heat anomalies at three transitions were measured, and the results are compared with the case of $BaTiO_3$.

DIELECTRIC measurements of $KNbO_3$ by Matthias and Remeika[1] revealed a ferroelectric Curie point at 435°C and a further transition at 225°C. An x-ray and optical study by Wood[2] revealed a cubic perovskite structure above the Curie point at 435°C, which transforms on cooling first to a tetragonal structure and then to an orthorhombic structure at the aforementioned two transition points. These transitions are related to the phase transitions in $BaTiO_3$ at 120°C and 0°C.[3] A further transition occurs in $BaTiO_3$ at $-80°C$, in which the structure changes from orthorhombic to rhombohedral. The above investigators found no significant change in the dielectric constant of $KNbO_3$ between room temperature and $-190°C$,[1] and no optical change was observed between 25° and $-50°C$.[2]

A preliminary dielectric study[4] carried out in our laboratory on $KNbO_3$ single crystals, prepared without flux, did show a sharp peak in the dielectric constant at $-50°C$ on cooling and $-35°C$ on heating, indicating the existence of a phase transition at this point. A further study has now been carried out on the dielectric, structural, and thermal properties of this lowest phase.

$KNbO_3$ single crystals were prepared as described by Wood,[2] using KCO_3 as a flux and cooling down from 1000°C. The crystals were generally rectangular, transparent, light yellow plates. Optical observation showed them to be multidomain crystals. Dielectric tests were made on crystals 2–3 mm on edge and about 0.3 mm in thickness.

Figure 1 shows the dielectric constant *vs* temperature curve measured at 10 kc/sec and a field strength of about 5 v/cm. The heating and cooling rate was about 1°C/min. In agreement with previous data, this curve shows a very sharp change in dielectric constant at

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* Owens-Illinois Research Fellow.
[1] B. T. Matthias and J. P. Remeika, Phys. Rev. **82**, 727 (1951).
[2] E. A. Wood, Acta Cryst. **4**, 353 (1951).
[3] See, for instance, A. Von Hippel, Revs. Modern Phys. **22**, 221 (1950).
[4] Pepinsky, Thakur, and McCarty, Phys. Rev. **86**, 650 (1952).