ON THE DIELECTRIC BEHAVIOR OF SELENIUM RECTIFIERS

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Introduction

It is well known that we cannot get the reproducible electric behaviors of semi-conductors for direct current, even if we get the purest samples as we can. It will be interesting to measure the dielectric constant of semi-conductors,[1] for we have the hope that the dielectric properties of semi-conductors could be measured reproducibly.

In semi-conductors in contact with metals, there is rectifying action. Using the recent theories of the crystal rectifiers[2] and of Mott and Schottky,[3] we can calculate the energy levels and impurity densities of the semi-conductors by the dielectric and static measurements.

Dielectric properties of the crystal rectifiers with the cat-whisker contact were measured,[2] but crystal rectifiers with the plane to plane contact have not been measured sufficiently. Then I used the selenium rectifiers in order to get the properties of semi-conductors at their surface.

The dielectric behaviors of selenium rectifiers were measured at different frequencies, temperatures and bias voltages. Some knowledges about the energy states and impurity densities at the surface of the semi-conductors were deduced from measurements. The rectifiers used for measurements were selenium rectifiers with various metal electrodes, i.e. barium, thallium, bismuth, cadmium and Wood's metal (the cadmium-bismuth-tin alloy).

The dielectric behaviors depend hardly on temperature except at the low frequencies and at the low bias voltages. The capacity and conductance of the rectifiers show dispersion of such a type as expected from the Goodman-Lawson-Sciff's theory.[4] The inverses of the squares of the capacities are in linear relation with the bias voltages satisfactorily.

Method of Measurements

The reactance variation method was applied to the measurement of capacity and conductivity. This method, although needs elaborate calculation, is the most precise

1) P. Henninger, Phys. Z., **39**, 911, 1938.

2) H. C. Torrey and C. A. Whitmer, *Crystal Rectifiers*, 1948.

3) N. F. Mott, Proc. Roy. Soc. (A), **171**, 27, 1939.
W. Schottky, Z. f. Phys., **113**, 367, 1939.

4) B. Goodman, A. W. Lawson, and L. I. Sciff, Phys. Rev., **71**, 191, 1947.

for the range of frequency to be measured.

Two selenium rectifiers of the same character were connected in the opposite direction, and were put in the tuning circuit with the variable air condenser and coil, being coupled with a powerful stable oscillator placed at distance sufficiently apart. Both ends of the tuning circuit were connected with the grids of a push-pull vacuum tube amplifier. The voltage drops of the a.c. across the resistances, placed in series between the plate circuits of amplifier tubes, were detected by the diode valves, and the rectified d.c. current was read by the galvanometer. The proportionality between the square of a.c. voltages across the tuning circuit and the deflections of galvanometer was tested at 60 cycles per second. I found that the a.c. voltage of about ten milivolts across the tuning circuit was sufficient to make the galvanometer deflect to the maximum.

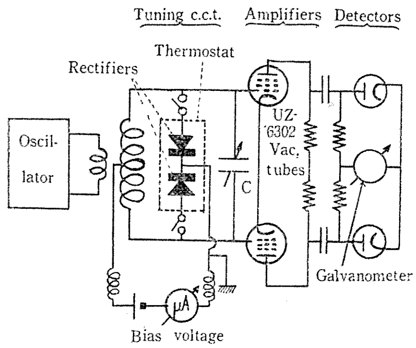

Fig. 1

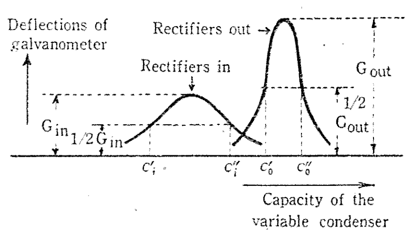

Fig. 2

The whole circuit is shown in Fig. 1. The selenium rectifiers connected with strips of short length are put in a thermostat. The inductance of the strips causes errors to the impedance values at the higher frequencies.

In our measurement, the capacity of the variable condenser was changed, and tuning curves were plotted for the two cases where the rectifiers were put in and out as shown in Fig. 2. At first, the maximum deflections were determined, and then the capacities corresponding to the half of the maximum deflections were determined from the tuning curves, with rectifiers in and out. We can get the capacity (C) and conductance (G) of one of the rectifiers as follows;[5]

$$C = (C_0'' + C_0') - (C_i'' + C_i'),$$
$$G = \omega[(C_i'' - C_i') - (C_0'' - C_0')],$$
$$G/\omega = (C_i'' - C_i') - (C_0'' - C_0').$$

C and G/ω correspond to the real and imaginary capacity of the rectifier as a dielectric, where ω is the frequency multiplied by 2π. Since I measured the static current of the two rectifiers in parallel, a half of the measured current gave the static current of a rectifier.

5) Cf., for example, L. Hartshorn and W. H. Ward, J. I. E. E., **81**, 597, 1936.

Samples

The process of preparing the samples was as follows: The iron discs plated with nickel were coated with the selenium, which was distilled in vacuum after chemical purification. The discs were then heated in the same way as it was treated in manufacture of the ordinary selenium rectifiers. Then the electrode metals were evaporated in vacuum on the discs. In this case, the films of most electrode metals covered the surfaces only in places as shown in Fig. 3, whereas the barium metal covered all over the surface of selenium by the explosion of barium azide in high vacuum. Further the Wood's metal was sprayed over the electrode metals in air as shown in Fig. 3.

The static characteristics of the rectifiers are shown in Fig. 4.

From the relation between the static current and the temperature, the activation energies were got. They are shown in Table 1. Because of the small range of temperature and the smallness of electrodes, the activation energies thus obtained are not sufficiently reliable. It is remarkable, however, that the rectifiers

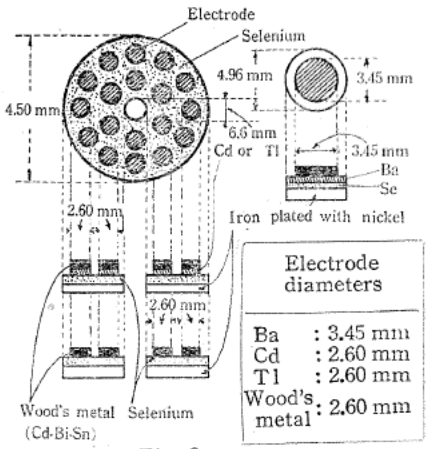

Fig. 3

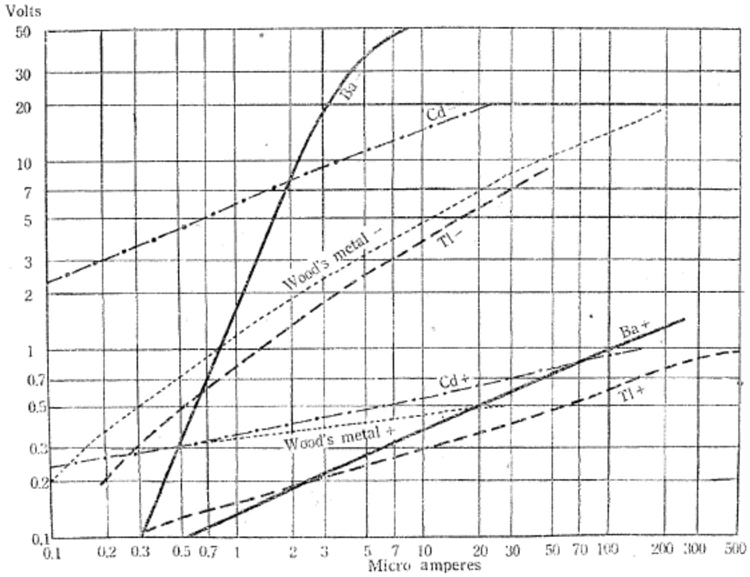

Fig. 4

with barium electrodes are the high-inverse back voltage ones and have distinct characteristics from those with other electrodes.

We should expect the constant activation energy $V_0 = \phi - \chi$ for the back voltage from the Mott's theory,[6] where ϕ and χ are the work functions for metals and semi-

6) N. F. Mott, loc. cit..

conductors respectively. The activation energy decreases at larger bias voltages, except in the barium-coated rectifiers.

We shall also expect that for the forward voltages higher than kT, the activation energies are nearly the same as for the forward voltages. At sufficiently high forward voltage, we should expect that the activation energies are a half of ΔE, where ΔE is the depth of the impurity levels below the conduction band of the semi-conductor. Fig. 5 shows the energy levels for metals and semi-conductors of the N-type which are not in contact.

Table 1

Bias voltage	Activation energy for various electrodes			
	Barium	Thallium	Cadmium	Wood's metal
Volts	eV	eV	eV	eV
−5	0.39	0.12	0.12	0.11
−2	0.43	0.17	0.18	0.18
−1	0.44	0.22	0.15	0.26
0.1	0.43	0.24	0.17	0.28
0.3	0.23	0.36	—	0.38
0.5	0.16	—	0.43	0.36

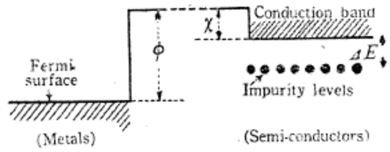

Fig. 5

Dispersion

The curves of capacity versus frequency, and G/ω versus frequency with different electrodes and at various bias voltages are plotted in Fig. 6 to Fig. 9.

The dielectric constant shows dispersion, where the rectifiers with barium electrodes have the relaxation frequency of about 50 kilocycles, and those of thallium, cadmium and Wood's metal are about 1,000, 100 and 1,500 kilocycles respectively.

The G/ω curves show peaks near the relaxation frequencies. These dispersion curves are in good agreement with that calculated from the theory.[7]

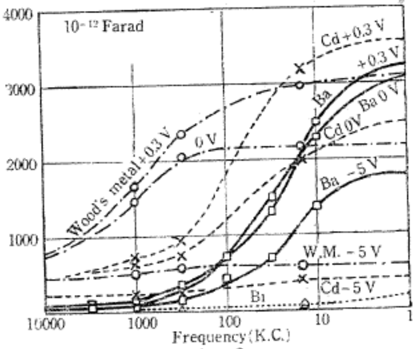

Fig. 6

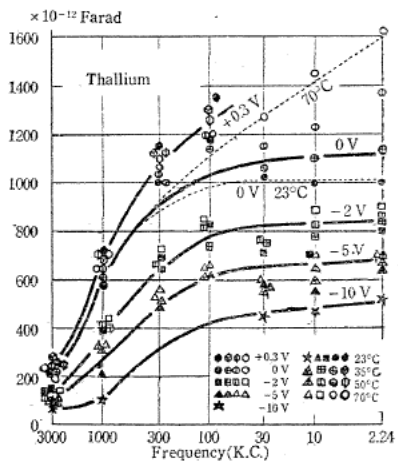

Fig. 7

7) H. C. Torrey and C. A. Whitmer, loc. cit., Chapt. IV-6, Fig. 4, 12.

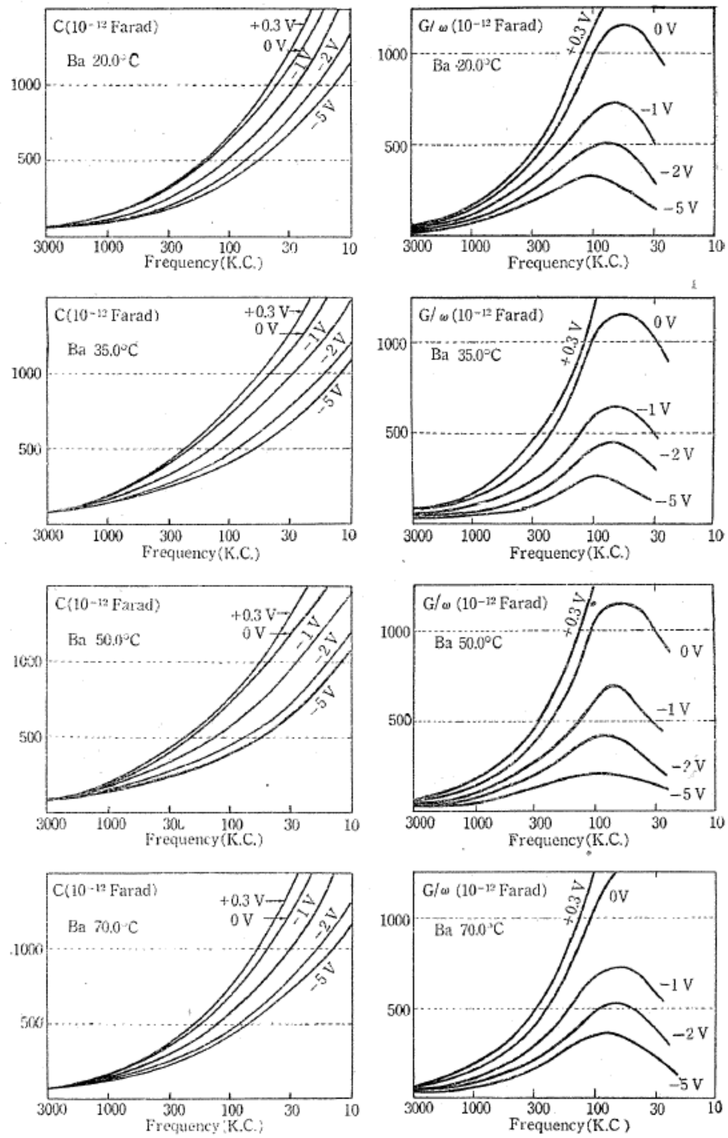

Fig. 8.

The relaxation frequencies lie between about 50 and 2,000 kilocycles, but these dispersion frequencies do not agree with the present theory. Goodman, Lawson and Sciff [8] calculated quantum-mechanically the ionization probability of the trapping electrons at impurity centres, using the model of deformable ions.[9] When ΔE is larger than $k\Theta_D$, where Θ_D is the Debye temperature for semi-conductors,[10] it is necessary

8) B. Goodman, A. W. Lawson and L. I. Sciff, Phys. Rev., **71**, 191, 1947. Cf. also H. C. Torrey and C. A. Whitmer, loc. cit., Chapt. IV–6.

9) R. Kubo calculated the ionization probability using more rigorous model (Papers presented at the annual meeting of the Physical Society of Japan on 11 May 1947).

10) Characteristic temperature for selenium diatomic molecules is 550∼570°K: Θ_D calculated from compressibility by the Einstein's equation is 639°K (0.060 eV).

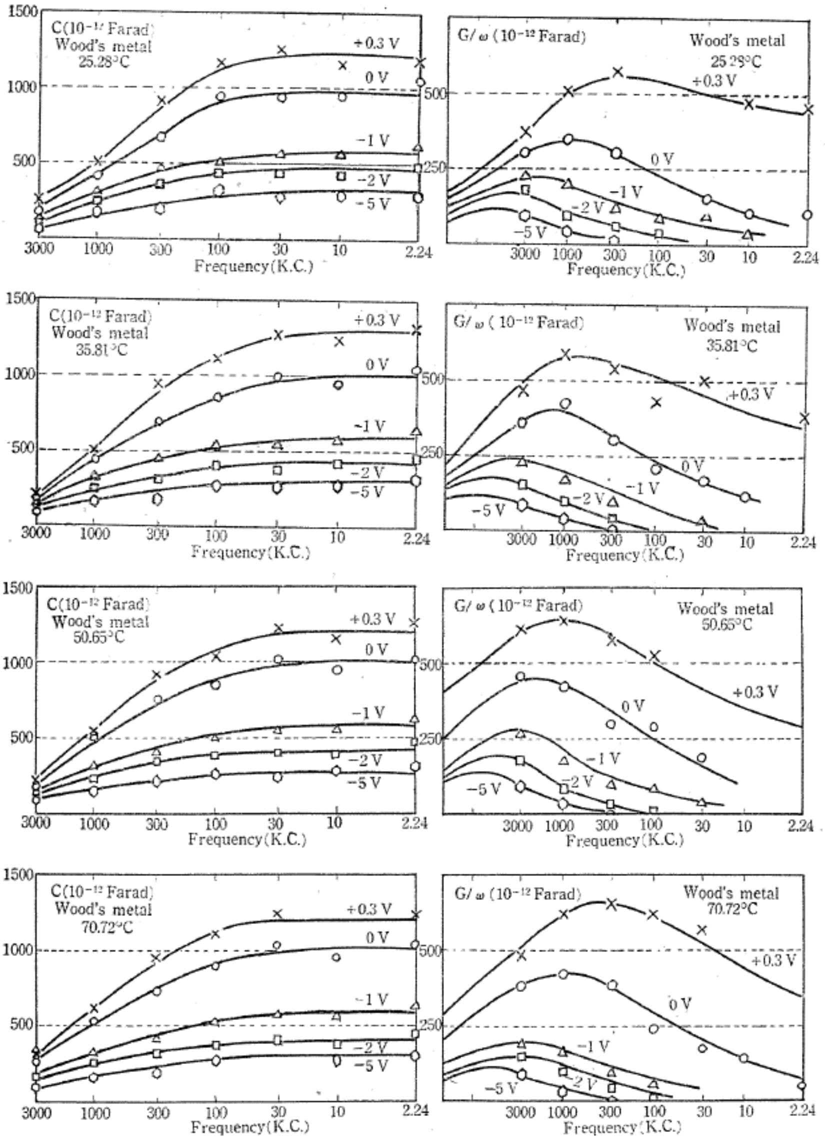

Fig. 9

for ionization to capture more than two phonons, and such is the case for the selenium rectifiers.[11]

They find in this case, the relaxation frequency is of about $10^6 \exp(-\Delta E/kT)$ sec^{-1}, which is far smaller than that obtained from the present experiment.

Bias Voltage Effect

The capacity of the rectifiers at bias voltage V is,[12]

$$C = (2A^2eN\varepsilon)^{1/2}(\phi_0 - V)^{-1/2},$$

11) In selenium rectifiers, ΔE is abont 0.2 to 0.9 eV for various electrodes.

12) H. C. Torrey and C. A. Whitmer, loc. cit., Chapt. IV-2. Equations (10), (15) and (16)

or $$C^{-2} = (2\,A^2 eN\varepsilon)^{-1}(\phi_0 - V)\,,$$

where ε is the dielectric constant of the barrier layer, A is the area of the rectifier, e is the elementary charge, N is the impurity density per unit volume and $\phi_0 = \phi - \chi - \Delta E$ as mentioned above.

From the experimental curve of C^{-2} versus bias voltage, we can determine the energy ϕ_0 and the impurity density N at the surface of the semi-conductors.

In Fig. 10 to Fig. 12, the curves of C^{-2} versus bias voltages are plotted, and they show a good linear relation to barium, cadmium and Wood's metal, but not to thallium. The values of ϕ_0 got from the figures are shown in Table 2, and the impurity

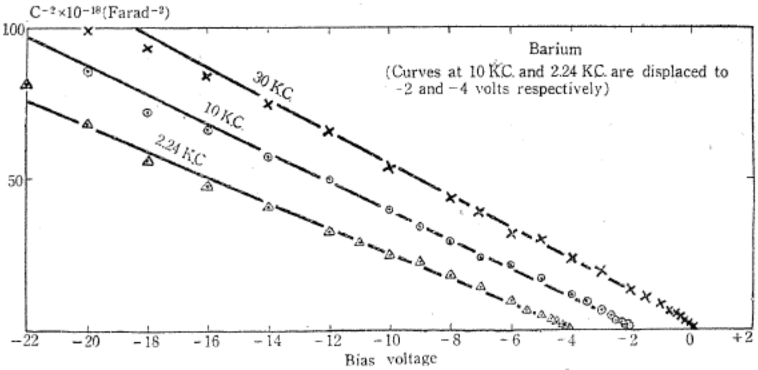

Fig. 10

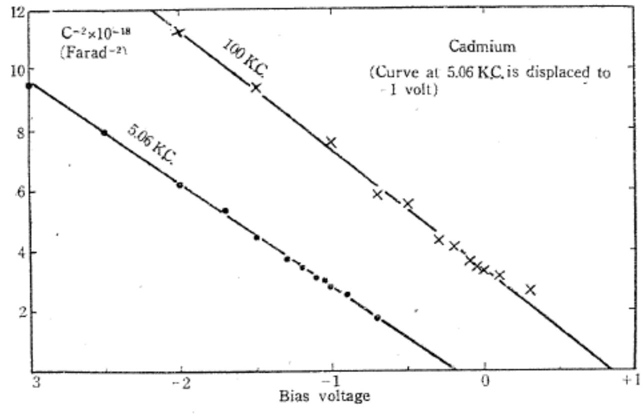

Fig. 11

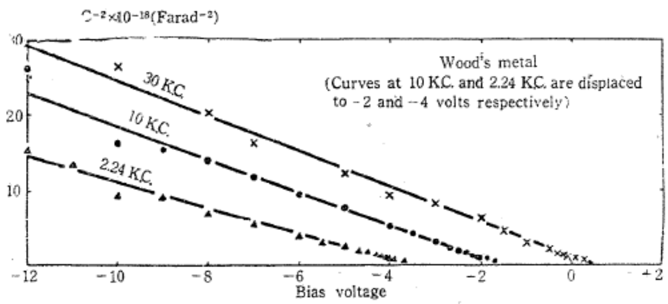

Fig. 12

density in Table 3 and in Fig. 13. ϕ_0 is nearly constant for cadmium and Wood's metal, but it increases at higher frequencies, and this increase may be due to the experimental error if I take ϕ_0 independent of frequency by the present theory.

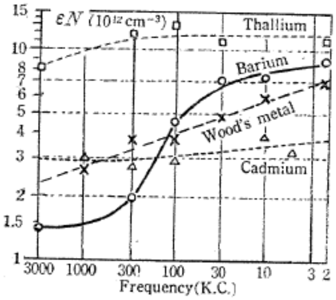

Fig. 13

Table 2

Frequencies (K.C.)	$\phi_0 = \phi - \chi - \Delta E$ for various electrodes. (electron volts.)			
	Barium	Thallium	Cadmium	Wood's metal
2.24	0.14	0.55	—	0.56
5.06	—	—	0.81	—
10.0	0.17	0.55	0.87	0.45
30.0	0.20	0.6	0.83	0.42
100	0.27	0.55	0.83	0.42
300	0.34	0.8	0.82	0.45
1000	0.34	0.9	0.94	1.2
3000	0.32	1.5	0.98	—
reliable values at low frequencies.	0.15	0.56	0.85	0.50

Table 3

Frequencies (K.C.)	Values of εN per cm^3 for various electrodes			
	Barium	Thallium	Cadmium	Wood's metal
2.24	8.8×10^{12}	11×10^{12}	—	7.05×10^{12}
5.06	—	—	3.40×10^{12}	—
10.0	7.5×10^{12}	—	3.95×10^{12}	5.95×10^{12}
30.0	7.2×10^{12}	11×10^{12}	4.00×10^{12}	4.75×10^{12}
100	4.6×10^{12}	13×10^{12}	2.85×10^{12}	3.70×10^{12}
300	2.0×10^{12}	12×10^{12}	2.75×10^{12}	3.75×10^{12}
1000	—	—	3.10×10^{12}	2.65×10^{12}
3000	1.4×10^{12}	8×10^{12}	—	—

Table 4

Temperature (°C)	Cadmium					
	$\varepsilon N(10^{12}\ cm^{-3})$			ϕ_0 (eV)		
	5.06 K.C.	30 K.C.	100 K.C.	5.06 K.C.	30 K.C.	100 K.C.
21	3.33	3.96	2.85	0.81	0.75	0.78
35	3.50	3.75	3.15	0.69	0.87	0.79
50	3.37	4.16	2.55	0.79	0.89	0.89
70	3.55	4.19	3.60	0.78	0.80	0.84

Temperature Effect of Dielectric Behavior

The static characteristics of rectifiers show the remarkable dependence on temperature, but the dielectric behaviors at high frequencies do not show such the temperature effect as at low frequencies and low bias voltages as we can easily find in Fig. 7 to Fig. 9.

At low frequencies, the conductance G approaches to that of the static character, and Fig. 14 shows the conductance G at various frequencies.

I cannot find any dependence of the values of ϕ_0 and εN on temperature within the experimental error, as shown in Table 4 for cadmium.

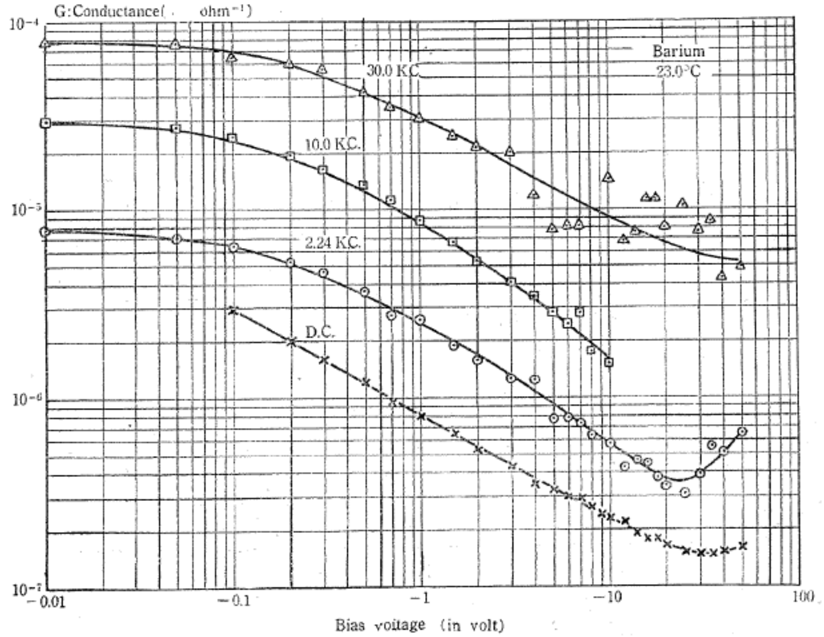

Fig. 14

Creeps and Agings of Selenium Rectifiers

Any quantitative measurements for creeps and agings were not made. As well known, the characteristics of rectifier depend on the previous history of them, namely the direction, the magnitude and the time of duration of the current passed through the rectifier. The prolonged passage of constant current for about an hour made the characteristic of rectifiers stable. In this way, the a.c. impedances could be got reproducibly.

When new bias voltage was suddenly applied after the prolonged and continuous application at certain bias voltage, the instantaneous increase or decrease of the a.c. conductance was found, and then decayed exponentially with times. Ordinarily, the application of new bias voltage for about an hour after the change of bias voltage was sufficient to make the a.c. impedances stable.

I observed the phenomenon of aging of the a.c. characteristics after the prolonged severe operation of rectifiers, that is, the impurity density N tended to decrease slightly, and the dispersion frequencies shifted toward higher frequencies. But the change of the values of ϕ_0 was not observed in our experiment of short duration.

There is inhomogeneity at the ionized or exhaustion layer. That is, most of the impurity centres are ionized at the surfaces of semi-conductors, but the density of the ionized impurity centres tails off towards the inside. At the given bias voltage, there is the stable distribution of the ionized densities. It takes the time to change from one distribution to another, each corresponding to two different bias voltages. In the transition between two equilibrium states, the current flows, and this phenomenon may be what is normally called the creep. It is just the same as the discharge or absorption current of dielectrics.

The density of the impurity atoms in selenium, which are diffused from the metal electrode as I later assume, may be in thermodynamic equilibrium with the electrode metal. The mean impurity density at the surface of selenium sometimes changes slowly corresponding to the change of temperature or because of electrolytic diffusion. This will be the phenomenon which we call the permanent change or aging.

The Structure of Barrier Layer

The above results show that the characteristics of the selenium rectifiers differ from electrode to electrode. Because of the irregularities of the activation energies shown in Table 1, the accuracy of the energy diagrams in Fig. 5 is not sufficient. The impulse measurements of more precision are needed for this purpose. It will be perhaps certain that the value of ΔE for selenium semi-conductors at the surface of rectifiers varies with the electrode metals. This fact tells us: the impurity atoms of the selenium are those of the electrode metal which have diffused into the selenium, and the impurity atoms are not contained previously in the selenium.

ΔE and ϕ_0 are small for barium electrode, that is, impurity level and the bottom of the conduction band are near the Fermi surface of metal as shown in Fig. 5. In cadmium and Wood's metal electrodes, ΔE is about 0.8 eV, and the difference between the characteristics of these two may be due to the change of work functions ϕ of the metals. χ may be the same in every case. This tells us that only cadmium atoms in Wood's metal are available for the formation of barrier layer.

The above results were based on the assumption that the theory of Mott [3] and the ionization theory of crystal rectifiers [2) 13)] are valid for the selenium rectifiers. The ionization theory of crystal rectifiers was completely inadequate for the explanation of dispersion frequencies of selenium rectifiers, although the shapes of the curves of dielectric constant versus frequency and G/ω versus frequency which I measured were just the same as the theory.[7] A new theory is needed for the explanation of the behavior of the selenium rectifiers of the plane to plane contact.

The Application of the Selenium Rectifier as the Variable Capacitance

It is no wonder that the dry rectifiers were used as condensers, because the elect-

13) B. Goodman, A. W. Lawson and L. I. Sciff, loc. cit.

rolytic rectifiers had been converted into electrolytic condensers.

The capacity of selenium rectifiers depended remarkably on the bias voltages. It was possible to serve the selenium rectifier as a variable condenser whose capacity was changed by the voltage regulation, or as a frequency modulator. Two rectifiers of the same character were connected in opposite direction, and they had the same electrical equivalence as a dielectric condenser with a grid between the two electrodes, whose capacity was varied with the grid potential.

The capacity of the barium-coated selenium rectifier could be varied in ratio of about one to one hundred, and was best suited for this purpose,[14] whereas those with cadmium and Wood's metal electrode varied only in ratio of about one to ten. With the push-pull vacuum tubes, it was possible to oscillate the waves of wide range of frequencies; the audio and intermediate frequencies using the rectifiers with cadmium electrode, and the audio frequencies using the barium-coated selenium rectifiers.

Frequency modulators will also easily be made. I think it will be possible to oscillate the a.c. without vacuum tubes using the variable capacitance, because transistor is a kind of variable resistor whose resistance is controlled by the foreign voltage applied, whereas the variable capacitance is a kind of variable capacity whose capacitance is controlled by the foreign voltage applied. It will be possible, with the help of tuning circuits and a transformer, to amplify the real part of voltage and fulfill an oscillating condition.

Conclusions

The impedance characteristics of selenium rectifiers at different frequencies, temperatures and bias voltages were measured. I observed the dispersion of capacity and conductance, and the effect of bias voltage on capacity. With the help of the theory of Mott and the crystal rectifiers, it was possible to determine the energy levels of semi-conductors in contact with metals. The theory of the crystal rectifiers was not adequate to the selenium rectifiers. I regarded the rectifiers as dielectrics, and I think it will be possible to explain many unknown complicated phenomena of rectifiers, for example, dispersion, creep and aging, by the introduction of the theories of dielectrics. But, the impulse measurements, the more exact impedance measurements and calculations for various electrodes, especially of the metals, the work function of which are known, are necessary.

The writer thanks Mr. K. Yosida of the Laboratory of Applied Science in Kyoto who prepared the barium-coated samples, and the Dengen Industrial Co. for the preparation and heat treatment of selenium.

14) Barium-coated rectifiers of large area and uniform character were difficult to prepare.