The Electrical Properties of Microcrystalline Selenium. I. Chlorine-doped Selenium

By Tsuneo ARAKI

(Received on May 10, 1962)

Several studies have been made of the electrical properties of micro-crystalline hexagonal selenium[1,2]. Most of them have dealt with pure selenium, iodine-doped selenium or bromine-doped selenium. The present series of studies has been undertaken to inquire into the effect of chlorine and metallic impurities on the electrical properties of selenium.

The conductivity of microcrystalline selenium changes greatly as a result of heat-treatment, because nucleation and the crystal growth occur in it[1,3]. In the present study, the electrical conductivity of chlorine-doped selenium is measured as a function of its crystallinity. The thermoelectric power and the capacity variation with various bias voltages were also measured for this substance, and the carrier concentration was calculated according to Schottky's theory.

Experimental

The selenium used in this investigation was purified from five-nine purity selenium obtained

---

[1] H. W. Henkels, *J. Appl. Phys.*, **22**, 1265 (1951).

[2] K. W. Plessner, *Proc. Phys. Soc. London*, **B64**, 681 (1951).

[3] H. Rebstock and K. O. Seilier, *Z. Naturforsch.*, **9a**, 49 (1954).

from the Mitsubishi Mining Co. The purification was carried out by the following steps: (1) oxidation with nitric acid, (2) treatment with ion exchange resin, (3) reduction with sulfur dioxide, and (4) distillation in vacuum.

This purified selenium was mixed with various quantities of selenium monochloride at 250°C and then quenched by pouring it onto a cooled marble plate to prepare amorphous selenium. The quantity of chlorine was measured by chemical analysis for each specimen, because some doped chlorine escaped during the heat-treatment.

Specimens used for the measurement of resistivity and thermoelectric power were prepared by the hot press method. Namely, chlorine-doped amorphous selenium was ground into powder of 80~120 μ and was pressed for 5 minutes under a pressure of 250 kg./cm^2. The pressing was done between two thin mica sheets placed on electrically-heated plattens which were thermoelectrically controlled at a temperature of 130°C. The shape of the specimen was a disk. 0.5 mm. thick and 10 mm. in diameter.

The specimen for the capacity measurement was pressed on an iron base plate which had been chemically etched and nickel-plated for the purpose of making ohmic contact. The procedure of the treatment was the same as in the hot press method described above. The thickness of the selenium of this specimen was about 0.1 mm. The specimen was crystallized by heat-treatment at 217°C, and then molten Cd-Sn eutectic alloy (m. p. 177°C) was sprayed onto the selenium surface, which was then used as a counter electrode. The simple barrier layer between the selenium and the counter-electrode alloy was formed by this procedure.

The measurement of electrical resistivity was carried out by the four-point probe method, and the Valdes correction was applied for the thin-sheet selenium[4]. A floating potential difference between inner probes was measured by a vibrating-reed voltmeter (internal resistance was about 10^{15} ohm), while the current through the outer pair of probes was about 5~10 μA.

The measurement of the resistivity of the specimen prepared for the capacity measurement was obtained from the voltage drop due to the current through the selenium layer. Results were in fairly good accord with those obtained from the four-point probe method.

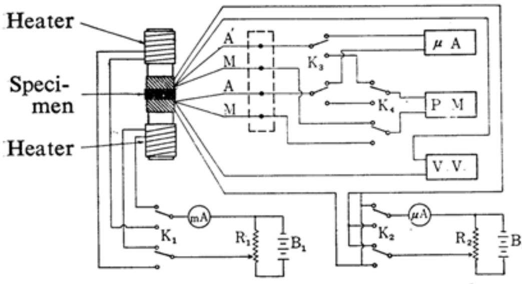

Fig. 1. Experimental arrangements for resistivity and thermoelectric power measurements.

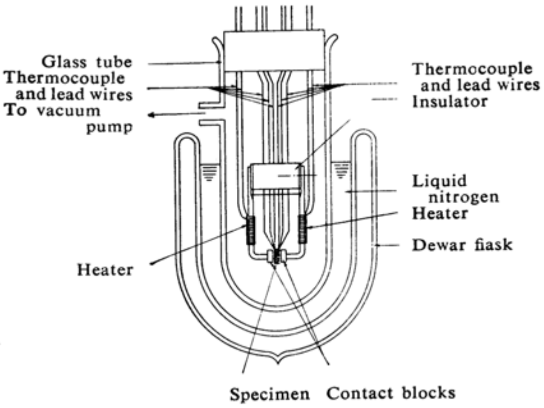

Fig. 2. Experimental arrangements for resistivity and thermoelectric power measurements.

The device used for the measurement of thermoelectric power and resistivity is shown in Figs. 1 and 2. The two points used for the measurement of thermoelectric power were arbitrarily chosen on both sides of the disk. The temperature difference between the two points was measured by an advance and manganin thermocouple. For the thermocouple, a wire homogenous in composition and small in diameter (0.12 mm.) was used, because these conditions reduced the errors due to the thermal conduction. Blocks in contact with the specimen were heated by 0.2-watt coils of of nichrome wire. The surfaces of the blocks were nickel-plated so that their good thermal and electrical contact with the specimen was protected. The temperature difference in a specimen was always maintained within 0.5~1.0°C, and the temperature was measured by a high sensitive potentiometer with an electronic galvanometer (7×10^{-11} A).

The thermoelectric voltage was determined from the measurement of the potential difference between the two advance wires, a high-sensitivity vibrating reed voltmeter being used. All the measurement heads were placed in a vacuum (about 10^{-3} mmHg) in order to reduce the thermal convection and the condensation of water in the measurement at a low temperature. The error in the thermo-electric power measurement was approximately 5 per cent, it was very difficult to maintain the reference junction within 0.02°C even if it was placed in a stirred ice-water bath. Since the resistivity of the specimen became very large at a low temperature, the charge which remained on the surface of the specimen afer the resistivity measurement produced an error in the thermoelectric power measurement. Therefore, these two measurements had to be carried out in different temperature cycles.

The capacity variation due to the bias voltage was measured by the substitution bridge method[5], in which a small AC signal (3 kc./sec., −30 db) was superimposed on the bias voltage.

---

[4] L. B. Valdes, *Proc. I. R. E.*, **42**, 420 (1954).

[5] H. Henisch, "Metal Rectifier", Clarendon Press, Oxford (1949), p. 48.

In order to investigate the effect of crystallization time, photomicrographs of the selenium surface were taken. The disk specimen prepared for the resistivity measurement was also used for this investigation.

Results

The results of the resistivity measurement for the specimens containing chlorine in various concentrations are shown in Fig. 3. In this figure, curves a, b, c and d show the resistivity of specimens which were kept for crystallization at 217°C for 0, 20, 60 and 500 min. respectively. The figure shows that there is a resistivity minimum in the curve for each heat treatment. The concentration of chlorine corresponding to the minimum changes with the duration of the heat treatment. The longer the heat treatment the lower the concentration. The observed values for the chlorine-free specimens were smaller than those reported by previous investigators[1,6]. This difference may have been caused by the effect of the atmosphere during the preparation. The specimens in the present experiment were treated in air because they had to be compared with those containing chlorine. Previous investigators had treated them in a vacuum. The present experiment shows that the atmospheric oxygen has some effect on the resistivity of chlorine-free specimens.

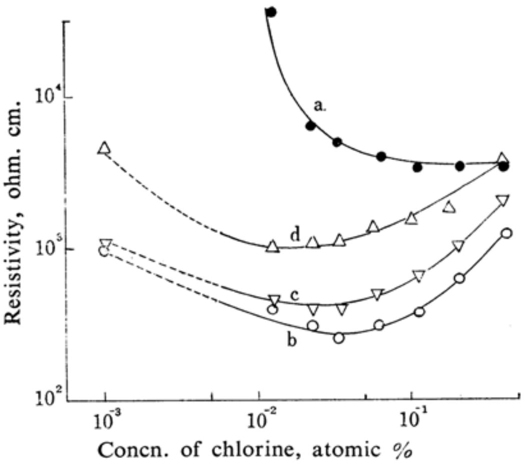

Fig. 3. Resistivity of microcrystalline selenium against chlorine content.

Figures 4 a—d show photographs of the surfaces of specimens which have been kept at 217°C for 20 min. Figures e—f shown photographs of chlorine-free specimens after various durations of heat-treatments, while g

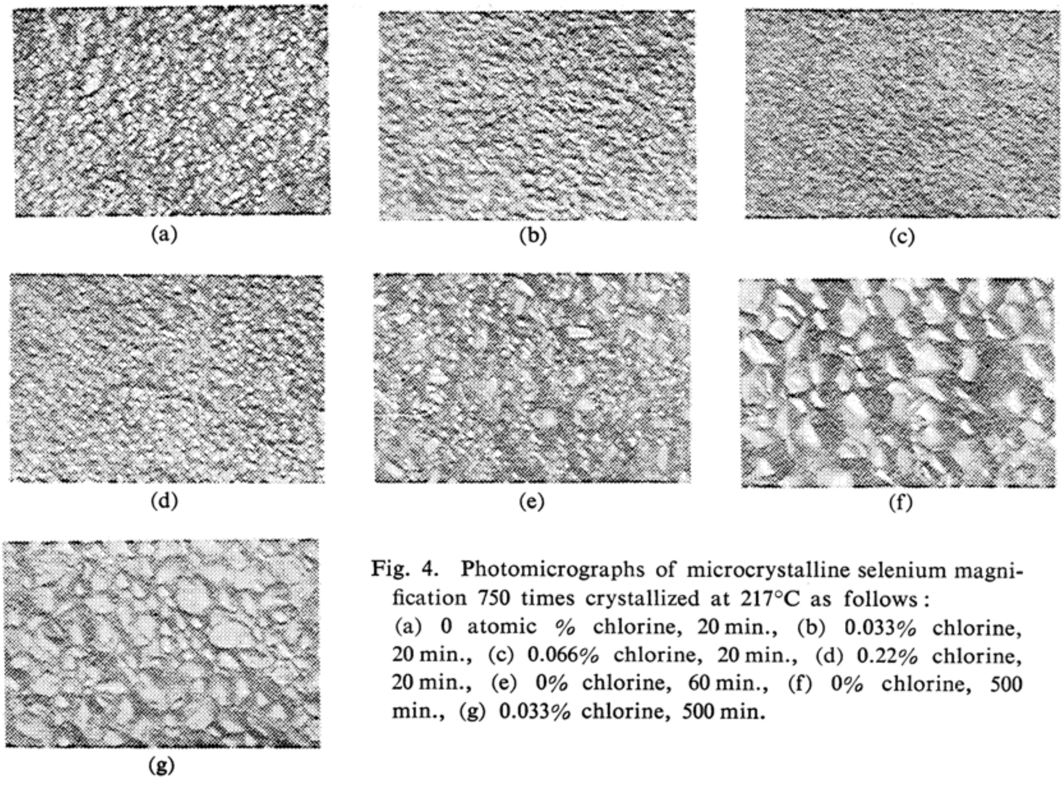

Fig. 4. Photomicrographs of microcrystalline selenium magnification 750 times crystallized at 217°C as follows:
(a) 0 atomic % chlorine, 20 min., (b) 0.033% chlorine, 20 min., (c) 0.066% chlorine, 20 min., (d) 0.22% chlorine, 20 min., (e) 0% chlorine, 60 min., (f) 0% chlorine, 500 min., (g) 0.033% chlorine, 500 min.

---

6) F. Eckart, *Ann. Phys.*, **14**, 233 (1954); **17**, 84 (1956).

shows a specimen after a 500-min. heat-treatment with the same concentration of chlorine as b. These photographs show that the higher the chlorine concentration, the smaller the grain size, and that the longer the heat treatment, the larger the grain size.

The thermoelectric power for semiconductors of the one-type, non-degenerate carrier is expressed by[7]:

$$Q=Q'+\frac{k}{e}\left[\frac{3}{2}\log T-\log n+\log\left\{\frac{2(2\pi mk)^{3/2}}{h^3}\right\}\right] \tag{1}$$

where k is the Boltzmann constant, n is the carrier concentration, m is the mass of the carrier, and h is the Planck constant. Q' is a number decided by the scattering of the carrier; usually 2 is given for this value for the selenium crystal with simple lattice scattering[8,9]. In the case of selenium containing much impurities, as in this experiment, a larger value of Q' should be used. However, in this report the value 2 was taken for the sake of simplicity. It is well-known that the carrier concentration, calculated from Eq. 1, is in fairly good accord with the results obtained from the Hall effect[9,10].

The carrier concentrations for the specimens were calculated from Eq. 1 and are plotted in Fig. 5. They are scarcely influenced by the chlorine concentration, and their values are in the range of $10^{16}\sim10^{17}/\text{cm}^3$.

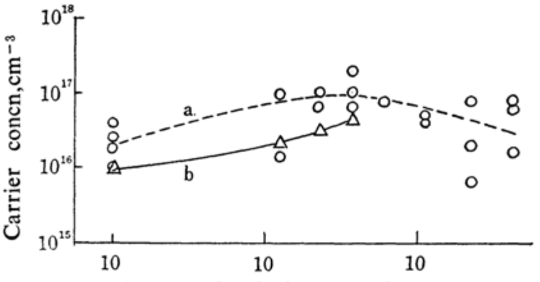

Fig. 5. Carrier concentration against chlorine content.

According to Schottky[11], the carrier concentration near a barrier layer is obtained by the equation:

$$n=2/KeF^2\,\mathrm{d}U/\mathrm{d}(1/C^2) \tag{2}$$

where $-e$ is the electron charge, F is the surface area, U is the bias voltage, C is the capacity of the barrier layer, and K is the dielectric constant. The dielectric constant for microcrystalline hexagonal selenium at 3 kc. has not yet been reported. In the present calculations, the value of 11 was used for this constant, which is obtained by extrapolation from the data of Hippel[12]. Most of the previous reports[5,13,14] used 6 for this value, but this figure is regarded as that for amorphous selenium.

According to Schottky's[11] theory, the relation between dU and d$(1/C^2)$ is linear for the simple contact between metal and semiconductor. However, it is actually not always linear in the measurement of selenium rectifiers, especially in the neighborhood of zero-bias voltage. Moreover, the relation changes with a lapse of time. The diffusion of the counter-electrode element to the selenium layer or the chemical reaction of these elements has been suggested as the cause of this change[15]. For this reason, the capacity measurement was carried out immediately after the counter electrode was applied.

The carrier concentrations obtained by the capacity measurement are plotted by curve b of Fig. 5. The values are somewhat smaller than those obtained from the thermoelectric power. The variation of specific resistivity with temperature is shown in Fig. 6. Curves, a, b and c, stand for the chlorine-free specimens crystallized by 20-, 60- and 500-min. heat treatments respectively. Each specimen increases

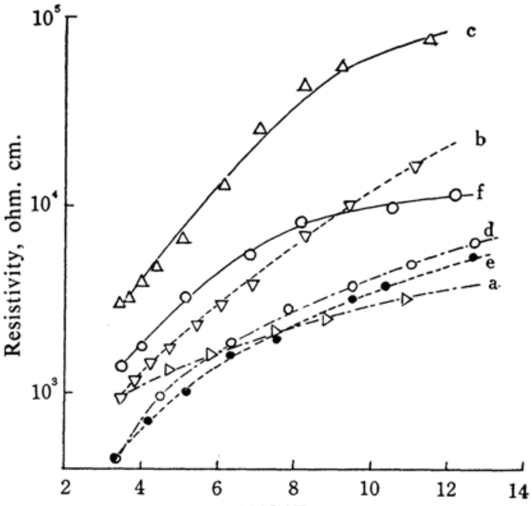

Fig. 6. Resistivity against temperature.

---

[7] V. A. Johnson, "Progress in Semiconductors I", Heywood, London, (1954), p. 68.

[8] H. W. Henkels, *J. Appl. Phys.*, **22**, 916 (1951).

[9] K. W. Plessner, *Proc. Phys. Soc.*, **B64**, 671 (1951).

[10] H. W. Henkels, *Phys., Rew.*, **77**, (1950).

[11] W. Schottky, *Z. Phys.*, **118**, 539 (1942).

[12] A. R. V. Hippel, "Dielectric Materials and Application", J. Wiley & Sons, New York, 301 (1954).

[13] E. Eckart and A. Schmidt, *Ann. Phys.*, **16**, 134 (1955).

[14] Y. Moriguchi and A. Okazaki, *Proc. Phys. Soc.*, **B70**, 991 (1957).

[15] J. Yamaguchi, *J. Phys. Soc., Japan*, **10**, 234 (1955).

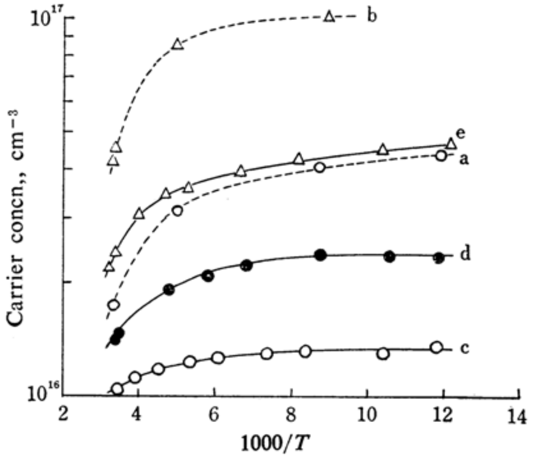

Fig. 7. Carrier concentration against temperature.

its resistivity at a low temperature. The resistivity does not change linearly with $1/T$. The gradient becomes slow at low temperatures. The gradient for the chlorine-free specimen becomes steep with the longer heat treatment, but that for the specimen containing chlorine was not so steep.

The carrier concentrations in the specimens after a 20-min. heat-treatment are shown in Fig. 7. Curves a and b show the results obtained from the thermoelectric power measurement of the chlorine-free and the chlorine-doped specimens respectively.

The temperature variation in carrier concentration obtained from capacity measurements is shown in curves c, d and e of Fig. 7. The results obtained from these two methods show nearly the same tendency. The gradient is steep at room temperature and becomes slow at a low temperature.

Discussion

The resistivity of selenium was at its minimum at a concentration of chlorine. The minimum value varied with the condition of the heat treatment, as is shown in Fig. 3. This fact has been noticed by Schweickert$^{16)}$, and the results of the present experiment are in good accord with his report.

According to the microscopic observation, the grain size of selenium was affected by the chlorine concentration and by the heat treatment condition, as is shown in Fig. 4. It is well-known that the crystallization usually depends on two factors; (a) the nucleation rate, and (b) the grain-growth rate. The fact that the grain size of the specimen containing chlorine is small shows that the contamination with chlorine promotes the creation of crystalline nuclei. On the other hand, the heat treatment increases the grain-growth rate. The crystallization of selenium from the amorphous to the hexagonal state decreased the resistivity at the beginning of the heat-treatment. However, the resistivity increased gradually again as a result of the long heat treatment. Schweickert has suggested that the chlorine was very loosely bound to the selenium and so was apt to escape from the surface of the specimen during the heat treatment. It was also seen that pure selenium increased its resistivity gradually as a result of the long heat treatment. Henkels$^{1)}$ suggested that the increase in resistivity is due to the purification process by crystal growth, while Rebstock and Seiler$^{3)}$ suggested that it is due to the decrease in inter-crystalline volume during the heat treatment.

The addition of chlorine did not increase the carrier concentration in selenium, which remained at an almost constant value in the range of $10^{16}\sim10^{17}/\text{cm}^3$. This tendency is similar to that reported in an experiment on selenium containing iodine or bromine performed by Henkels$^{1)}$ and Plessner$^{2)}$.

According to the measurements by Henkels$^{8)}$ and Plessner$^{9)}$, the selenium single crystal prepared from the liquid or vapor phase had a carrier concentration in the range of $10^{13}\sim10^{14}/\text{cm}^3$. Plessner considered that the acceptor centers in selenium did not consist of "impurities" in the form of foreign atoms, but only of imperfections in the selenium crystal lattice. He also considered that most of the chlorine atoms doped in selenium were concentrated in the grain boundary and had an effect on the mobility. However, the mobility calculated from the resistivity and the carrier concentrations is less significant.

According to Nijland$^{17)}$, the carrier concentration obtained from the Hall coefficient corresponds to the value of a well-conducting phase; on the other hand, that obtained from thermoelectric power corresponds to the value of a low-conducting phase which surrounds the well-conducting phase. Meanwhile, the carrier concentration obtained from the capacity variation due to bias voltage is that near the barrier layer or that in the space-charge transition region itself. Henkels$^{11)}$ reported that the carrier concentration of selenium obtained from the capacity measurement was not in accord with that obtained from the thermoelectric power or from the Hall coefficient, but details were not reported in his paper.

---

16) H. Schweickert, *Z. Phys.*, **128**, 47 (1950).

17) L. N. Nijland, *Philips Res. Rep.*, **9**, 259 (1954).

According to Moriguchi[18], the carrier concentration, which was obtained from the capacity measurement for the commercial selenium rectifier, decreased at low temperatures. Therefore, he considered that the mechanism of the barrier layer in the rectifier was very complicated and was not suited for the calculation of its carrier concentration. However, the carrier concentration obtained from the capacity measurement in the present experiment increased at low temperatures, This result was in fairly good accord with that obtained from the thermoelectric power. The present agreement seems to come from the methods of preparing the specimens. Both specimens were prepared from the same selenium material, and the measurement of capacity was carried out immediately after the application of the counter electrode for the purpose of avoiding the formation of other complicated barrier layers.

The resistivity of all the specimens for the present experiment increased at low temperatures. However, it was doubtful whether this resistance was caused by the real bulk resistivity of selenium. The resistance showed departures from Ohm's law at the low fields, and it was supposed that there were some barrier layers. Rebstock and Seiler[3] reported that the resistivity of microcrystalline selenium measured at a high frequency was not so much increased at a low temperature; they considered that the increase of DC resistivity at the low temperature was caused by the grain boundary of microcrystalline selenium. For these reasons, the apparent decrease in mobility calculated from the resistivity and the carrier concentration, especially at a low temperature, might not occur in the bulk phase but might be caused by the intercrystalline structure.

Summary

1. The resistivity of microcrystalline selenium doped with chlorine was changed by heat treatment. The results were in fairly good accord with the measurements obtained by Schweickert. Selenium doped with chlorine had the same characteristics as that doped with iodine or bromine.

2. The results of microscopic observation showed that the grain size became smaller with the higher chlorine concentration. This tendency was similar to that found in iodine- or bromine-doped selenium.

3. The resistivity variation with temperatures below room temperature was affected by the heat treatment of the specimen. The effect was greater for the specimen free from chlorine.

4. Carrier concentrations were obtained from the measurement of capacity and also from the thermoelectric power. These two methods gave results which were in agreement with each other. The concentrations were shown to be increased at low temperatures.

The author wishes to express his thanks to Dr. Takehiko Shimanouchi of The University of Tokyo and to Dr. Juichi Osawa, Dr. Yukimatsu Takeda, Dr. Sueo Hattori, Mr. Yoshinori Mihara and Dr. Yoshiro Moriguchi of his company for their kind advice throughout this work. The author is also grateful to Mr. Shuzaburo Imai and to Mr. Makoto Saito for the preparation of specimens.

Semiconductor Engineering Department
Electronic Components Joint Division
Nippon Electric Company
Kawasaki

---

[18] Y. Moriguchi, *Kurume Univ. Journal* (*Nat. Sci.*), 6, 9 (1955).