Resistivity of Evaporated Tellurium Films

Resistivity of Evaporated Tellurium Films

Takemaro SAKURAI and Seiji MUNESUE

The Research Institute for Scientific Measurements

(Received December 15, 1951)

Synopsis

The tellurium film was made by the vacuum evaporation and its resistivity was measured at various temperatures. When the substrate was kept at the room temperature during evaporation, the film showed a $\log R - 1/T$ curve, conspicuously different from that of the bulk. By the heat treatment or by the electron bombardment, the resistivity was found to change irreversibly, becoming nearer to that of a bulk specimen. These features were explained by the crystallization of the amorphous deposit in the film. On the other hand, when the tellurium was deposited on a hot substrate, about 470°K in temperature, the resistivity of the film was found to be in good accordance with that of the bulk, giving the activation energies of 0.34 and 0.04 eV in the intrinsic and the extrinsic range, respectively.

I. Introduction

From the researches recently done, tellurium is considered to be a semi-conductor with the activation energy of from 0.34 to 0.38 eV in the intrinsic range. The physical properties of this material are very interesting subjects in the field of the study on semi-conductors but reports concerning them are extremely few in number. In some of the experiments to investigate these properties, thin evaporated films are used as specimens. For example, in the observation of the absorption spectra in the infra-red region, which is being projected by the present writers, evaporated films must be used because of a large extinction coefficient. It must be noticed here that the properties of evaporated films are, somtimes, far different from those of bulk specimens. Such being the case, the results obtained will be inadequate to be available to the theories on semi-conductors, built on the basis of crystallized materials. Therefore, it seems worthwhile to make clear whether the properties of tellurium films are different from those of bulk specimen or not, and, if so, to try to find out a method to make a film, same in its properties as a bulk specimem. From this point of view, the writers investigated the resistivity of evaporated films, taking into consideration the procedure of deposition, treatment and other outer conditions. The experimental details and the results obtained will be described in the following sections.

II. Experimental procedure

The tellurium used in this experiment was purified first by the chemical method and then by the vacuum distillation. The chemical procedure of purification was performed by Prof. H. Tominaga at the chemical laboratory of this university. The apparatus used for the vacuum distillation is shown in Fig. 1. A silica tube, 1.2 cm in inner diameter, 70 cm long and wrung at several portions to make nodes,

was covered with an iron pipe and inserted into an electric furnace, so that the tellurium at the bottom be placed at the center of the furnace. The iron pipe

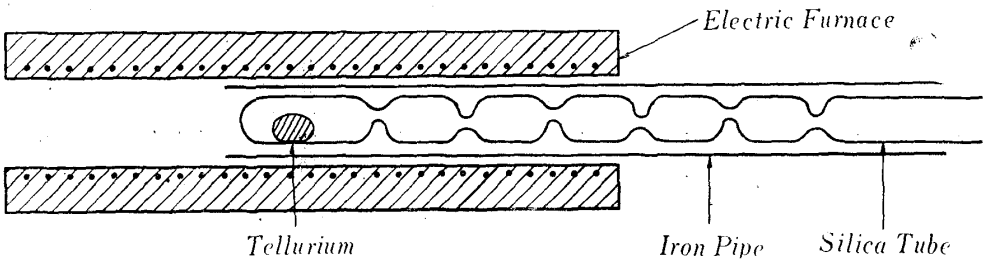

Fig. 1. Apparatus for the vacuum distillation.

served effectively to give a suitable heat gradient along the silica tube. By this arrangement, it was possible to make the tellurium deposit at a limited portion of

Fig. 2. Spectrograms of tellurium specimens.
(a) before vacuum distillation,
(b) after vacuum distillation.

the tube, and other impurities on both sides, separately from the tellurium. In order to test the efficiency of this method, the specimen wich contained considerable amount of impurities was distilled and examined by the spectral analysis. It was found that the impurities were eliminated exceedingly by single distillation, as is seen in Fig. 2. The tellrium, purified by chemical procedure, was distilled several times and was ascertained to be spectroscopically pure.

The evaporation was performed using the vacuum tubes of two kinds which are schematically shown in Fig. 3. In the apparatus illustrated in Fig. 3 (a), the tellurium was evaporated from a tungsten filament F and was deposited on a substrate S. The substrate could be heated by an adjacent heater H to observe the resistivity at various temperatures which were measured by a junction J. The heater

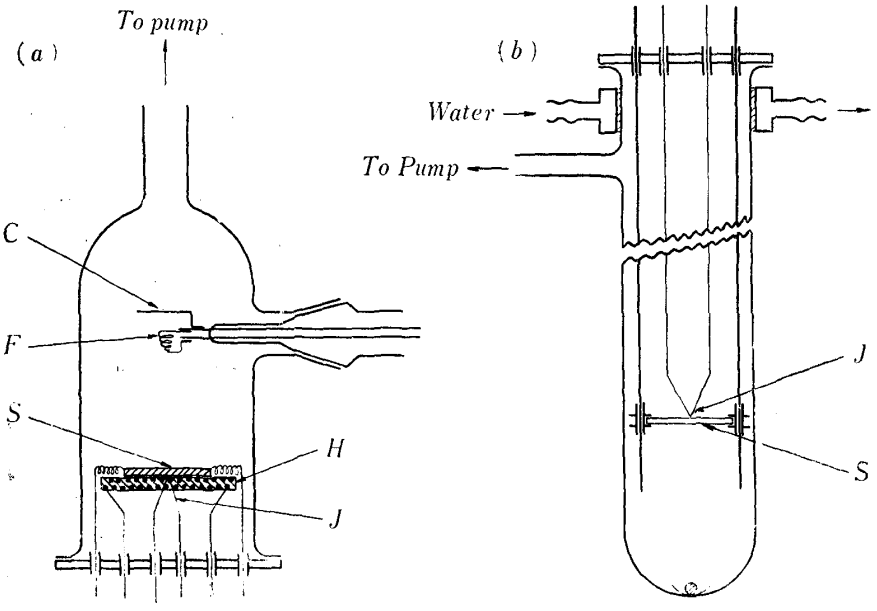

Fig. 3. Evaporation tubes.

was made by winding a nichrome wire on a silica plate, coarsely in the center and closely at the ends in order to get the homogeneity of temperature in the substrate, and by covering it with mica and copper plate. When the electron bombardment for the deposited film was desirable, the filament F was used as a cathode and the high tension wihch would be applied to the film was supplied from a neon transformer. If the specimen still remained after evaporation, it should be evaporated out before electron bombardment, covering the film with a screen C by turning a stem of a filament with a side tube. Another evaporation apparatus was constructed of Pyrex-glass tube, 5 cm in diameter and 50 cm in length, in which a substrate and a junctin were set as is shown in Fig. 3 (b). In this case, the specimen was placed at the bottom of the tube and was evaporated by heating from outside with an elctric furnace. By adjusting the distance between a substrate and a specimen and by displacing a furnace, the substrate was kept at a desired temperature during evaporation. In the observation of resistivity, the temperature of substrate was changed by heating the tube with an electric furnace or dipping it in liquid air.

As a substrate, a silica plate, 35 mm long, 7 mm wide and 2 mm thick, was used. Both ends of the plate were coated with Aquadak to make electrodes for the film. In preparation, the substrate was washed with soap and water, dipped in an aqueous solution of caustic soda and swabbed with nitric acid. Then it was cleaned by exposing it to a glow discharge during evacuation and heating it in high vacuum for a long time, prior to evaporation.

Most of the films used for the measurement were those with the thickness of from 200 to 5,000 A. Supplying an electric potential of several volts from the battery to the film, the current was measured by the micro-ammeter or the galvanometer of direct reading type, from which the resistivity was obtained. In some cases, the potentiometer was used also to measure the resistance.

III. Results obtained

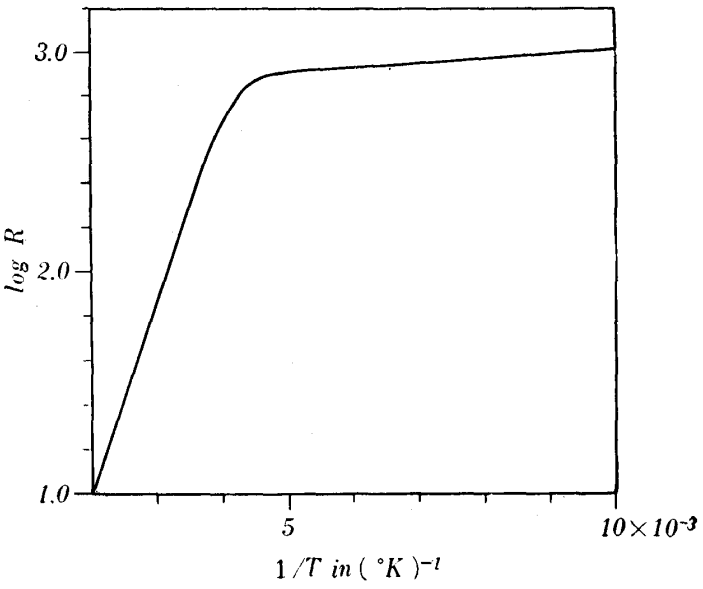

Fig. 4. Resistivity curve of a bulk specimen.

As this experiment was to investigate in what manner the electrical behavior which tellurium possesses as a semi-conductor would change in the case of evaporated films, it was necessary to know first the properties of bulk specimens. Therefore, a specimen was cut from the well crystallized sample which was used for evaporation, and its change of resistivity with temperature was measured. In Fig. 4, the result obtained is illustrated. This

figure shows that tellurium is a semi-conductor, intrinsic at high temperature and extrinsic at the temperature lower than about 230°K. The activation energies in the intrinsic and the extrinsic range measured were 0.34 and 0.01 eV, respectively.

It was found, in the course of this experiment, that the electrical properties of evaporated films were much affected by the temperature of substsate during evaporation. For convenience' sake, the results obtained will be divided into those where the substrate is cold and those where the substrate is hot, of which the former will be described first. When the substrate was not heated during evaporation, the film deposited showed high resistivity immediately after the evaporation, but resistivity decreased with time and reached a finite value as shown in Fig. 5. The

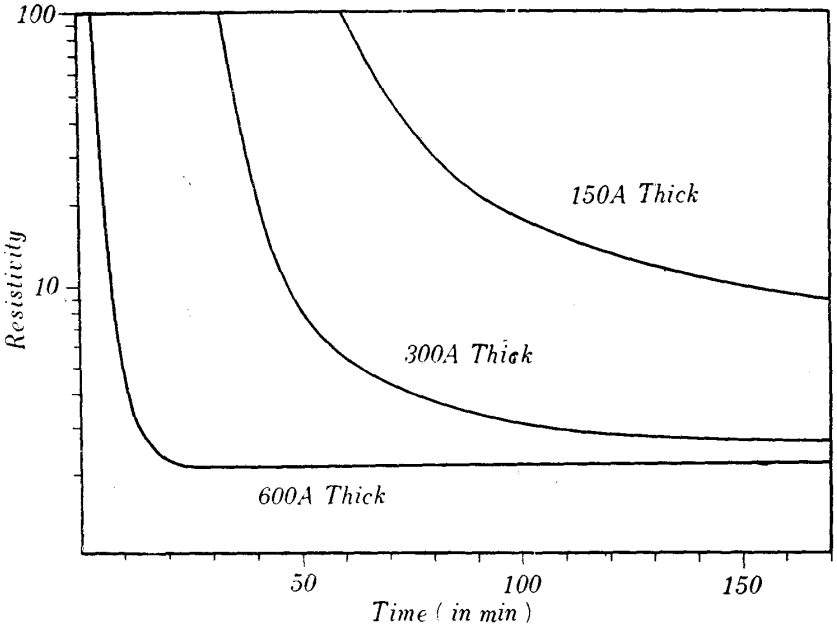

Fig. 5. Change of resistivity after the evaporation.

thinner the film was, the longer was time required to reach saturatoin. Even if the electric potential, applied to measure the resistance, was cut off for a short duration, no anomaly was found in the resistance-time curve. Therefore, the change of

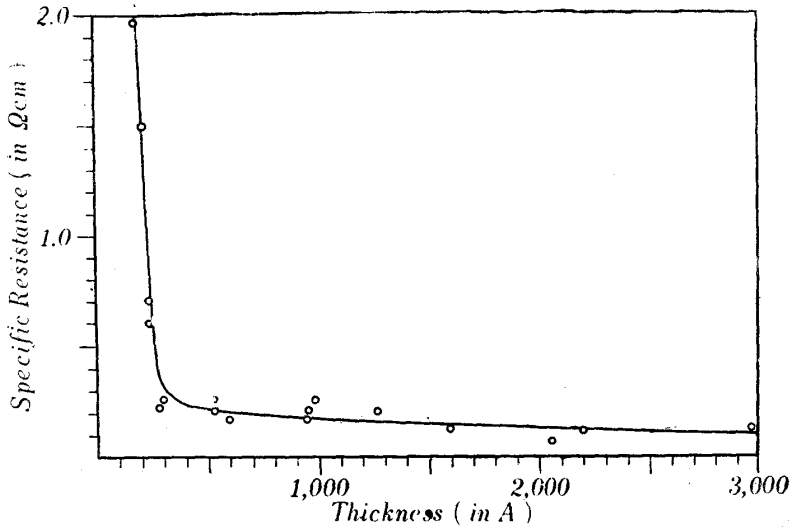

Fig. 6. Change of specific resistance with the thickness of evaporated films.

resistivity seemed not to be attributed to Joule's heat by the electric current. In Fig. 6, the saturated specific resistance is plotted against the film thickness. It must be noticed here that the resistance suddenly increases when the thickness becomes less than 300 A.

Raising and lowering the temperature, the change in resistivity was observed for various films. Starting from the room temperature, the rise in temperature produced a decrease in resistance which was accompanied by a considerable time lag when the heating was rapid, as is seen in Fig. 7. Therefore, the measurement was made by heating the film very slowly, the result of which is exemplified by the curve A-B in Fig. 8. Lowering the temperature, the resistance increased not along the curve A-B but along the curve B-C, indicating the heating course A-B to be irreversible. The course B-C was entirely reversible and no time lag was perceptible even for a rapid heating in this region. If the temperature was raised higher, however, the change in resistivity became irreversible again and time lag was introduced but for a slow heating. In general, the resistivity changed irreversibly as long as the temperature was raised above that at which the film had been placed, but reversibly at the temperature at which the film had been put or lower. Moreover, the decrease in inclination and the increase in curvature of resistivity curve were seen in successive reversible courses, finally reaching the limited values.

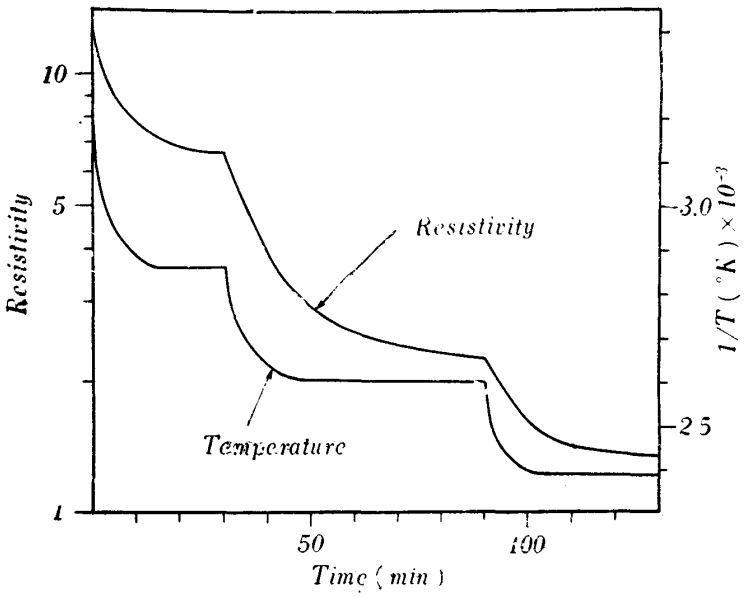

Fig. 7. Change of resistivity in rapid heating.

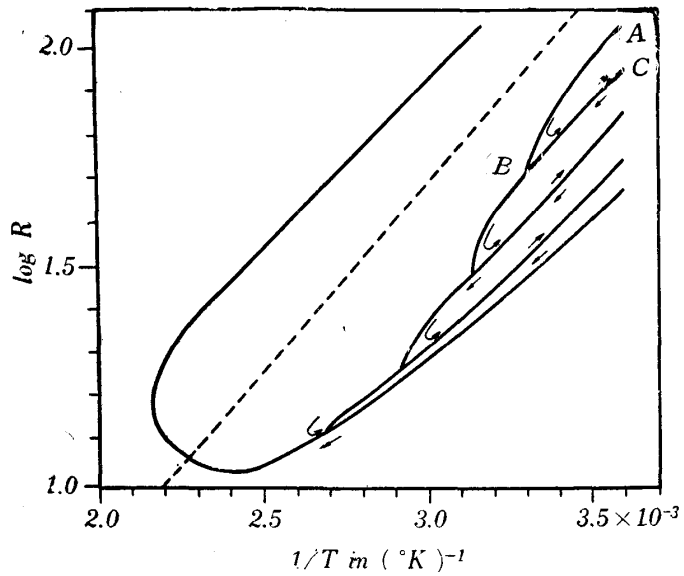

Fig. 8. Resistivity curve of the film deposited on a cold substrate. Dashed curve is that obtained by a bulk specimen.

It was found that the resistivity R in the reversible course could be expressed by the equation by putting a suitable constant r,

$$\ln(R-r)=E/2kT+\text{Const.}$$

where E is the activation enrgy of bulk specimen 0.34 eV. From the change of resistivity curve in successive reversible courses, it was deduced that by raising the temperature above that to which the film had been subjected, the value of r increased and approached a maximum. The value of r/R was nearly the same for the films with the thickness larger than 1,000 A but was less for thinner films. If the temperature was raised to about 450°K, a sudden increase of resistance set in, and by lowering the temperature, the decrease of r, hence, the approach to a bulk specimen, was observed. This feature was conspicuous for thinner films.

In order to see whether the effect which the film suffered in the heat treatment would be given by other method or not, the deposited films were bombarded by the electron beam for a fraction of a minute immediately after evaporation. The applied potential and the total current were 10,000 V and 1 mA, respectively. In this case, the change of resistivity with temperature was reversible up to about 400°K, and the constant r showed a large value. Therefore, the electron bombardment seemed to give an effect, similar with that which was given by the heat treatment.

The results, described above, was obtained by placing the film in vacuum. When the air was introduced in the evaporation tube, the resistivity was seen to change to a considerable degree. When the air pressure was raised by step, the resistivity decreased with time and reached a saturated value at a given pressure; further decrease occurred with increasing pressure. By evacuation, large part of the decreased amount remained without being recovered. The films, treated by the electron bombardment, showed a large effect compared with those which were not treated. The results obtained with the fiims with various thickness are reproduced in Fig. 9. As seen in this figure, the thinner the film was, more conspicuous the effect was. Furthermore, the log R-$1/T$ curve of the film, placed in the air, was found to give a slightly larger value of the constant r than that which was obtained in vacuum. With oxygen, nitrogen, hydrogen and carbon dioxide, similar effect was also observed. The ratio of the resistivity at the pressure of 760 mm Hg to that in high vacuum were plotted against the film thickness for various gases, but no peculiarity for any sort of gas could be found, which markedly exceeded the experimental error.

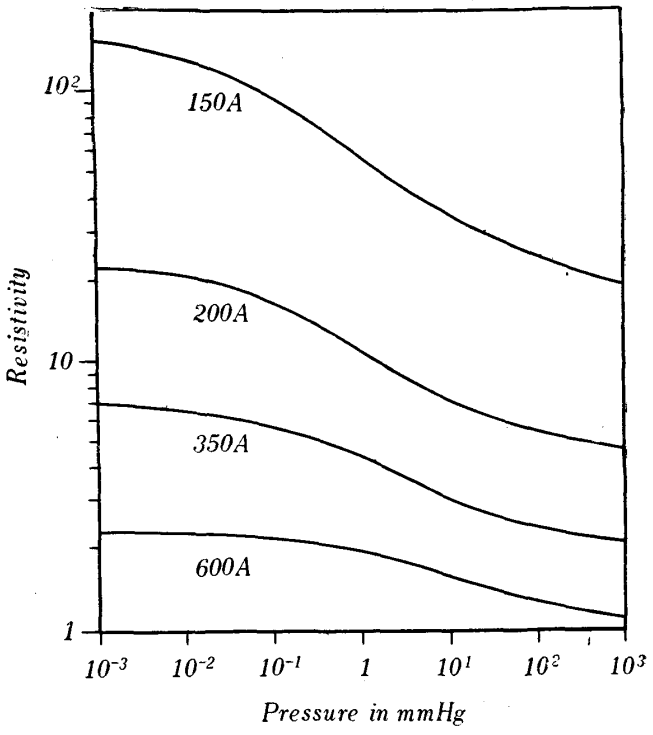

Fig. 9. Effect of air on the resistivity.

It was made clear in the above that the properties of a film, deposited on a cold

substrate, was conspicuously different from those of bulk specimen and that, by heat treatment or electron bombardment, they approached those of the bulk, but considerable discrepancies were found between the two. These features were found to be the same even for a film with the thickness of 50μ. It had been found that tellurium, deposited in distillation tube, was crystallized beautifully. This fact suggested that the well crystallized film would be obtained by heating the substrate during evaporation. Therefore, the films were deposited on the substrate, kept at the temperature of about 470°K or higher, and their resistivities were investigated. In this case, the change of resistivity with temperature was entirely reversible without any time lag from the beginning, and the effect of gas could not be observed. The $\log R$-$1/T$ curve, obtained with the film with the thickness of 5,000 A, is illustrated in Fig. 10. Comparing the curve with that of a bulk specimen in the same figure, the transition point from the intrinsic to the extrinsic range of the film is displaced towards higher temperature, but the activation energies of the film in the intrinsic and the extrinsic range are 0.34 and 0.01 eV, respectively ; hence an excellent accordance is found between the two. For the films with various thicknesses, the values of the activation energy in the intrinsic range were nearly the same, while those in extrinsic range were slightly larger, giving the mean value of 0.04 eV.

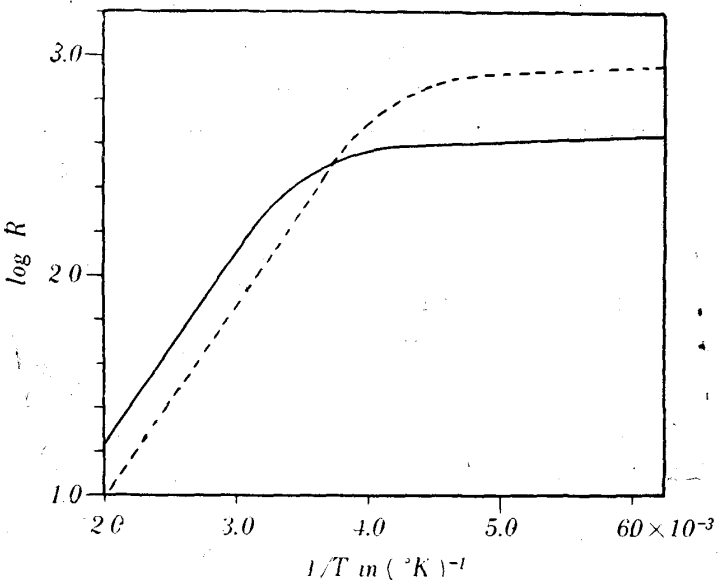

Fig. 10. Resistivity curve of the film deposited on a hot substrate. Dashed curve is that obtained by a bulk specimen.

IV. Interpretation of results obtained

When the tellurium is deposited on a cold substrate, it seems that the atoms arrived reach the thermal equilibrium with the substrate by the transference of their kinetic energies. Atoms deposited may wander to make micro-crystals by the energies of their own or of the atoms which arrive after, but soon the energies for wandering will be lost through the substrate. Hence, the films deposited are of such nature that micro-crystals are buried by amorphous deposit. As the resistivity of amorphous deposit is high, the film will show a large value of resistance. Seeing from the change of resistance after evaporation, the crystals seem to grow larger with time and reach an equilibrium at a definite temperature. In this case, the resistance of the film R is to be given by the sum of the resistance of micro-crystal, a semi-conductor, and that of the amorphous deposit r which is large in value and has a small temperature coefficient. Therefore, the resistance R is

expressed by the equation

$$R = Ae^{\frac{E}{2kT}} + r,$$

where E is the activation energy of micro-crystal, or approximately by

$$\ln(R-r) = E/2kT + \text{Const.},$$

as the variation of $\ln A$ with temperature is small.

By raising the temperature above that at which the film has been placed, crystals grow larger and reach a new equilibrium state, while at the temperature at which the film has been put or lower, the equilibrium remains unchanged. By this, the reversible and irreversible courses in the $\log R$-$1/T$ curve and the time lag in the irreversible courses by rapid heating are well explained. Growth of crystals and diminish of amrphous portions associated will result in the decrease of resistance. By the migration of atoms, however, small empty spaces grow in amorphous portions; this is thought to be the reason why the value of r increases in successive reversible courses. For thinner films, the atoms may migrate easily, hence, smaller value of r/R will be obtained. By further heating, the empty spaces will grow larger, but, at the same time, amorphous portions crystallize rapidly, and the whole film becomes nearer to a bulk crystal. A sudden change of resistivity at 450°K can well be interpreted from such a viewpoint.

The effect of the electron bombardment is thought to be the same as that of the heat treatment, except that the energy for crystallization or migration is supplied from the kinetic energy of electrons. In order to confirm it, a thin evaporated film was examined by means of the electron microscope. It was found that the tellurium atoms migrate to make crystals and that small empty spaces grow in the film. It was also observed by means of the electron diffraction that amorphous deposit crystallized rapidly by exposing it to the electron beam.

As to the effect of gas on the resistivity, any reasonable interpretation has not yet been given. As this effect is large for the film, treated by electron bombardment, and is nil for those deposited on a hot substrate, it seems that the amorphous deposit is affected by the gas which has entered small spaces. Seeing from the increase of the constant r, it is hardly acceptable to think that the amorphous deposit crystallizes by the pressure of gas. It may be possible that tiny amorphous portions become conductive by absorbing the gas or affected by the gas from outside. But it is also doubtful whether the inertness of effect for the sort of gas is allowed or not, under this consideration. For the confirmation of this, further research will be neccessary.

On the other hand, when the substrate is kept in high temperature, atoms deposited have sufficient energy to wander to make crystal in the whole course of evaporation; hence, the largest part of the film is well crystallized. The agreement of activation energies betweem the evaporated film and the bulk specimen is thought to be a good evidence for this consideration. The shift of the transition point towards higher temperature and small enhancement of activation energy in the extrinsic range in the case of the evaporated film might be ascribed to the crystal

imperfection. Recently, W. Scanlon and K. Lark-Horovitz[1] measured the resistivity of evaporated layer and obtained resistivity curves which show the activation energy of 0.039 eV at low temperature and go through a maximum, followed by a rapid decrease of resistance in the intrinsic range giving the activation energy of 0.36 eV. T. Fukuroi, S. Tanuma and S. Tobisawa[2] also investigated the electromagnetic properties of single crystal and found that the resistivity increased with $1/T$, showing the activation energy of 0.34 eV in the intrinsic range, but slightly decreased in the extrinsic range. Therefore, the measured activation energy in the intrinsic range 0.34 eV shows an excellent agreement with the values obtained by others. The observed activation energy in the extrinsic range agrees with that obtained by Scanlon and Lark-Horovitz but the maximum of resistivity has not been found in the present investigation. The obtained curve in the extrininsic range differs from that by Fukuroi and his collaborators also, as the reversal of inclination is found between the two. If the low temperature resistivity is given by the sum of the resistivity due to scattering by lattice ions, and by impurity ions as was pointed out by V. A. Johnson[3], above discrepancies may be ascribed to the disagreement of the relative magnitudes of these two resistivities. With a technique of purification and an accuracy of analysis, attainable at present, such a disagreement may be admissible. Moreover, it is thought that the interpretation of results, above mentioned, will never be damaged by these discrepancies. Thus, the evaporated films, prepared by suitable procedure, are quite the same as a bulk specimen from the view of the electrical resistivity and the other experimental data obtained with them seem to be available as well as those by bulk specimens for the theories on semi-conductors.

In conclusion, the writers wish to express their deepest appreciations to Prof. H. Tominaga, the director of the Glass Research Institute, for the purification of tellurium, to prof. T. Hibi, for the facilities of the observation by the electron microscope and the electron diffraction and to the Ministry of Education, for the Grant in Aid for Fundamental Research.

(1) W. Scanlon and K. Lark-Horovitz, Phys. Rev., **73** (1948), 1256.
(2) T. Fukuroi, S. Tanuma and S. Tobisawa, Sci. Rep. RITU, **A 1** (1949), 373.
(3) V. A. Johnson, Phys. Rev., **74** (1948), 1255.