ON LEAD TELLURIDE RECTIFIERS. II

ELECTRICAL FORMING IN P-TYPE SPECIMEN

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I. Introduction

In the previous paper,[1] which will be referred to as "paper I" hereafter, we showed that P-type crystal of lead telluride has a rectifying character after it is properly treated, and gave some features of the rectifier but did not give detailed relations between the treatments and the consequent characteristics. In this paper we report some experiments on electrical forming of P-type lead telluride rectifier. It is shown that with increasing forming current in the forward direction the rectifying power of the crystal becomes larger although the crystal shows only little rectifying power before forming.

The experiments reported here are made on the effects of the magnitude of the forming current, of the time during which the current flows and of the direction of the current. The fact that the reverse current does not make the rectifier so good although the forward current makes it appreciably better shows that the field effect may not be ignored in the forming effect. These informations, we hope, will contribute something to studies of rectifiers of intermetallic compounds.

II. Experimental Procedures

The crystal used was the same as described in paper I. We used a tungsten wire as the cat whisker and the cleaved surface of the crystal as before, and other experimental procedures, unless otherwise stated, were the same as those in paper I.

The forming was made using the circuit as shown in Fig. 1. The magnitude of the forming current was controlled by adjusting the resistance R_1 so as to make the current reach a desirable magnitude. The time during which the current flowed was adjusted by varying the resistance R_3 and by changing the switch S_3. The routine procedure of experiments was as follows. The whisker was pressed by a screw to the cleavage plane with the pressure of 2 grammes weight, and a current flowed, S_1 being switched on, in the circuit excluding the timer, and it was adjusted to a desirable magnitude by adjusting R_1. Then S_1 was switched off and the whisker was detached, and again it was touched with the same pressure. We confirmed that the current flowing after the above procedures was satisfactorily the same in magnitude as the adjusted current, except for very small current. And then the forming was made by using the timer, changing the switch S_1 to it. Measurements were made by changing the switch S_2. The next measurement was done after taking off the whisker and again touching it and forming, that is to say, each run including the forming process was made independently.

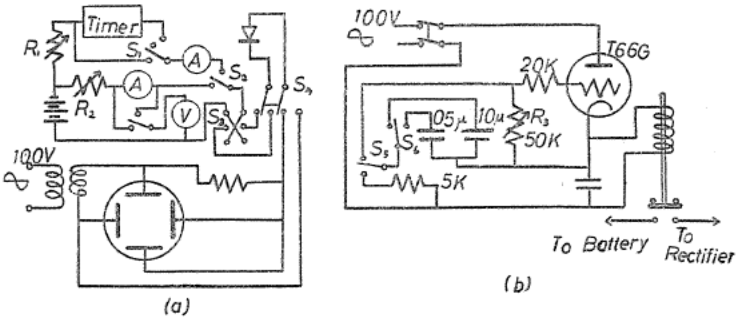

FIG. 1. (*a*) Circuit for forming and measurement, (*b*) Timer.

The experiments extended from 1/6 to 10 seconds in time duration, up to 100 mA in magnitude of forming current and for both forward and reverse directions.

III. Results

(*a*) *Forward Direction.* The effects of current which flows in the forward direction are described. The results may be thought to be affected by the experimental conditions such as the pressure of the whisker and the condition of its tip. The effect of the pressure was surveyed and found not to be so important for the characteristics in pressure range in the neighbourhood of 2 grammes weight.[2] The whisker used in these experiments was all the same and not sharpened during these experiments. The characteristic values obtained by the experiments are not very divergent for the same values of forming current and of time duration.

The crystal shows little rectifying power when the whisker touches simply, but, after forming by passing a current in the forward direction, rectification takes place. The curve representing the v-i characteristic before forming is not linear but its deviation from a straight line is small, and the asymmetry of it with respect to the origin is small for small voltages and it becomes appreciably large for larger voltages. After forming the curve takes the form suitable for crystal rectifier, namely, the current in the forward direction increases rapidly with increasing voltage for small voltages and then almost linearly with an increasing rate which is larger than that before forming; in the reverse direction the curve representing the v-i characteristic at smaller voltages is concave upward as that in the forward direction for smaller voltages, and the curve becomes, for larger voltages, a horizontal line or a line slightly inclined to it.

The forward resistances generally decrease with increasing forming current, and are more divergent in magnitude for smaller forming current than for larger current. The mean values of the effective resistance, that is to say, the ratio of voltage to current for respective voltages are shown in Fig. 2 as a function of forming current. The resistances for larger voltages reach a saturation value for 50 mA forming current as seen in Fig. 2. The figure also shows that the resistances for smaller voltages decrease at first with increasing forming current but they do not become so small at larger forming current as those for larger voltages. They seem to have a maximum at 70–80 mA forming current. This corresponds to the fact that the current, after forming with 70–80 mA, is rather small at several hundredths of a volt and then rapidly increases with increasing voltage.

The reverse resistances after forming with forward current are not so definitely characterized by forming process as forward resistances, and are divergent in their magnitude. The resistances resulted from the forming are in some cases very high and in a few cases low. But general tendency can be recognized. The mean values of the reverse resistances corresponding to those of Fig. 2 are shown in Fig. 3. It is noticeable that the resistances do not simply decrease with increasing forming current.

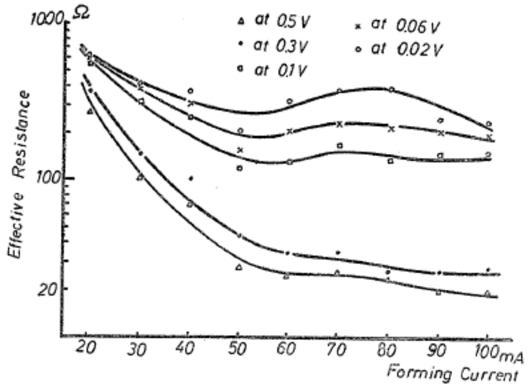

FIG. 2. Effective resistance in the forward direction after forming with forward current.

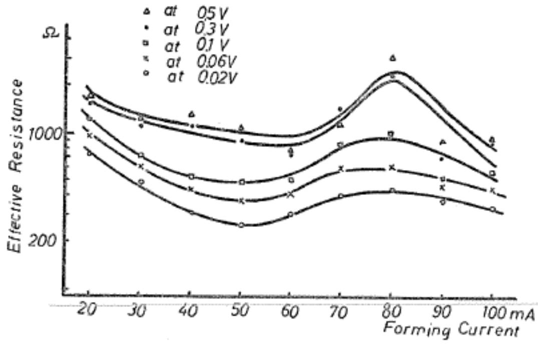

FIG. 3. Effective resistance in the reverse direction after forming with forward current.

The reverse current of crystal rectifier consists generally of three components, i.e. saturation (diode), ohmic components and other component increasing rapidly with voltage. The *v-i* characteristic curve before forming is irregular and not distinctly recognized to be consisting of these components. The saturation and linear parts come to appear definitely by forming. After forming with forming current of more than 50 mA the current flowing in the reverse direction is sometimes practically constant from several hunderdths of a volt to about a volt, which is frequently obtained with 70–80 mA forming current. The best values obtained for them are shown in Table 1. With forming by near 100 mA forming current the third component, which increases rapidly with voltage, becomes dominant sometimes at even several tenths of a volt. Therefore by forming of larger current large reverse resistances and consequently large rectification ratios sometimes are obtained, and small values of them also obtained occasionally.

The mean values of the rectification ratio at respective voltages and for respective forming currents are plotted in Fig. 4. Up to 80 mA, the larger the forming current is the larger the ratio becomes. For 90 and 100 mA forming current the ratio becomes smaller than that for 80 mA. These are due to the decrease of the reverse resistance.

The spreading resistance and the height of the rectifying barrier obtained as in paper I are shown in Fig. 5. The height of the barrier is about 0.14 ev. in the mean value with 0.01 ev. as probable error. The values of the sperading resistances after forming by larger current are about 15 Ω and these values well agree for respective formings as seen from the probable error in the figure.

The values of the above figures and tables are those obtained when the time during which the current flows is one sixth of a second. Experiments were made

TABLE 1. Statistical Values of the Effective Resistance and Rectification Ratio after Forming with Forward Current

	Effective resistance in ohms				Rectification ratio	
	Forward direction		Reverse direction			
	at 0.1 V	at 0.5 V	at 0.1 V	at 0.5 V	at 0.1 V	at 0.5 V
Forming current	50 mA					
Mean value	120	28	490	1,200	5.1	43.5
Standard deviation	44	6	130	590	2.7	26.1
Max. value	210	44	1,000	3,300	14	148
Min. value	72	21	350	560	1.7	12.5
Forming current	70 mA					
Mean value	170	27	890	1,200	4.5	59.7
Standard deviation	45	11	640	600	2.6	48.4
Max. value	290	52	2,500	2,500	8.8	159
Min. value	120	15	250	500	2.0	16
Forming current	80 mA					
Mean value	140	24	1,000	3,200	9.2	233
Standard deviation	60	10	570	2,900	6.0	196
Max. value	250	41	2,000	10,000	10.8	713
Min. value	59	9	330	390	1.2	26
Forming current	100 mA					
Mean value	150	20	580	890	4.7	42.6
Standard deviation	44	2	121	200	2.2	10.0
Max. value	210	23	830	1,200	8.2	60.6
Min. value	65	16	470	555	2.4	28.4

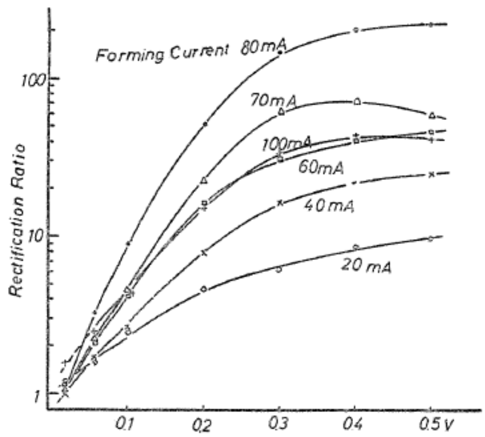

FIG. 4. Rectification ratio at respective voltages after forming with forward current.

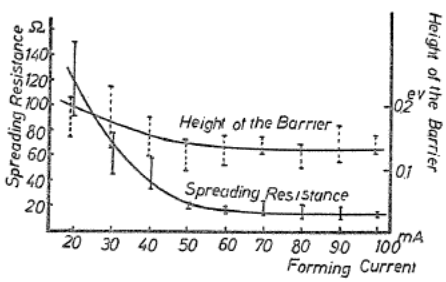

FIG. 5. Variation of spreading resistance and height of the barrier with forming process.

for other time duration of 1, 5 and 10 seconds, but no regular variation was discovered within these experiments.

The difference for various whisker materials was surveyed and no appreciable difference was found as mentioned in paper I.

(*b*) *Reverse Direction.* The effects of current which flows in the reverse direction are given. A current of several mA passing through the rectifier in the reverse direction, which corresponds to the voltage slightly lower than the peak back voltage, makes the reverse resistance grow gradually larger as stated in paper I. A larger current in the reverse direction does not improve the rectification power.

As for the reverse current, experiments were made for the combination of 20, 50 and 70 mA in current and 1/6, 5 and 10 seconds in time duration. The *v-i* characteristics after the above currents flow are similar to the ones before forming although the resistances generally become smaller. The characteristics are nearly ohmic for small voltages, and there are no saturation components in the reverse direction and no exponential increases in the forward. For larger voltages, increase of current becomes more than linear. Rectification ratio is very small especially for small voltages. These characteristics only show P-type behaviour, that is to say, when the whisker is negative the current is almost always larger than when it is positive, and for larger voltages the former is always larger than the latter.

For smaller flowing current the consequent resistances for short time duration are larger than those for long time duration, but for larger current they are not so different. These results are shown in Figs. 6 and 7 in the mean values.

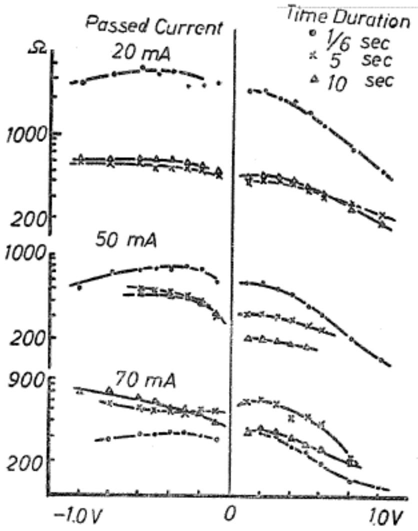

FIG. 6. Effective resistance after passing a reverse current.

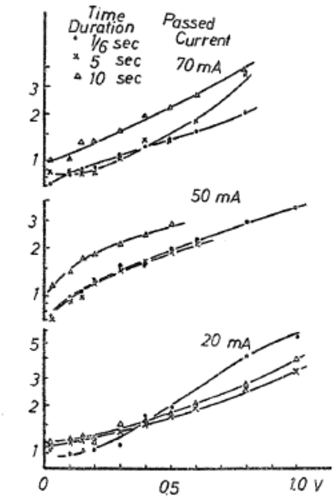

FIG. 7. Rectification ratio after passing a reverse current.

IV. Discussion

The details of rectification phenomena have not been fully understood, and the theories cannot explain the phenomena quantitatively. The forming process, therefore, is not so clear enough. Many experiments and interpretations of forming have been made with germanium and silicon concerning both rectifier and transistor.[3] Some attempts[4] to overcome the discrepancies between the early theories and experimental results have been done. The multicontact theory,[5] one of these attempts, assumes that the height of the barrier at the metal-semiconductor contact varies from spot to spot and endeavours to reduce these discrepancies especially for the value of α which is expected theoretically to be e/kT (refer to Eq. (1) of paper I).

The causes of improving the rectifying characteristics by electrical forming may be attributed principally to thermal effect, field effect and their combination. Being heated by Joule effect at the contact the current will affect the contact in the following ways: it changes the state of the crystal near the contact by introducing traps or acceptors thermally produced, or vice versa; donors or acceptors near the contact are made to move easily, temperature being raised, by diffusion or electric field; whisker and semiconductor become in close contact with each other by being heated. Moving of ions and consequent change in the distribution of donors and acceptors are thought to be field effect. It is enhanced by Joule heat at the contact.

The decrease of forward resistance after forming with forward current is thought to be due to the fact that the contact becomes closer by heating. Especially the spreading resistances, calculated from the slope of the straight line, approach the same value for larger forming current, although for smaller forming current their magnitudes are divergent. This fact can be explained by the above heating process, as the spreading resistance is to be $\rho/4r$, r being the radius of the contact.[1] When the contact is not perfect, r can be considered to be effectively small and is different in magnitude in respective cases; when the contact becomes closer by heating, r becomes effectively larger and perhaps approaches the same value. The fact that the resistance after passing a current in the reverse direction becomes smaller than before can be thought to be caused by the same heating effect.

Electric field, whose direction is such as to make current flow in the forward direction, can move the acceptors, in P-type specimen, from exterior toward interior; if donors are present they move in the opposite direction. When this movement occurs the barrier will change in the sense such that the height and width of the barrier become larger. It is assumed, as made in the multicontact theory, that the height of the barrier at the contact between whisker and surface of P-type lead telluride crystal varies from spot to spot. and moreover N-type barrier may be there, and at some spots contact is not perfect. By these assumptions the fact, that in the v-i curve before forming there is no saturation component and is little rectification and that the resistance is large, can be understood.

The following phenomena can be explained if we assume that, by the forming with forward current, the height of the barrier of each spot becomes larger, the width of it thicker, N-type barriers, if exist, are changed to P-type ones and hence the barrier of the contact becomes more uniform. The phenomena are as follows: there appears the saturation component by the forming process; the voltage at which the third component begins to be predominant becomes rather high; the reverse resistance becomes sometimes very high in spite of decrease in the forward resistance. These are because the linear component and the component which increases rapidly with voltage are thought to originate from spots of low barrier or thin barrier or barrier of inverse type. We may expect, therefore, that ohmic and third components become larger when the barrier is low in the height and thin in the width, or the barrier is of inverse type, that the saturation component becomes larger and the other components become smaller when the barrier is high and thick and moreover uniform. The fact that the large reverse current does not improve the rectifier is thought to be due to the direction of its field. Reverse field, which is large enough to cause the field effect, may affect the barrier in such a way that its effects are opposite to those caused by forward field, namely, the rectifier is made worse.

If the current is expressed by $I=I_s\{\exp(\alpha V)-1\}$, as the theories require (the notations are referred to Eq. (1) of paper I), the ratio of forward and reverse currents for the same voltage is proportional to $\exp(\alpha V)$. The semilogarithmic plot of the ratio versus voltage gives the value of α from the slope of the resulting curves. The curves in Fig. 4 are seen to be nearly linear at small voltages and the values of α obtained from the slope are tabulated in Table 2. This shows that the value of α becomes larger when the magnitude of the forming current is larger. This fact also can be explained by the consideration that the height of the barrier becomes larger and more uniform. The reason is as follows. If there are spots at the contact whose barrier heights are different from one another, the total current through the contact increases exponentially at small voltages, but the increasing rate is smaller than that theoretically expected. This is the result of the multicontact theory. If the height of the barrier is constant throughout the contact, the exponential increasing rate is to be e/kT as ordinary theories show. We expect, therefore, that the more uniform the barrier becomes the nearer to the value theoretically expected the increasing rate rises.

TABLE 2. The Variation of the Value of α with Forming Process

Forming current (in mA)	20	30	40	50	60	70	80	90	100
α	—	—	11	13	14	16	20	12	13

In connection with the decrease of the reverse resistance by the large forward current we notice that by condenser discharge through Pt-PbTe contact we get a welded non-rectifying contact with the resistance of several ohms.

V. Summary

We investigated the electrical forming process. It is shown to be possible to improve the rectifying characteristics with forward current forming. Some data on the effects of the magnitude of the forming current and of time duration are presented. On the other hand the reverse current does not make the characteristics so good as the forward current does. These experimental results can be interpreted qualitatively on the basis of the multicontact theory.

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References

1) Y. Sakaki, K. Shogenji, Y. Un-no, S. Uchiyama and Y. Sugiyama: Mem. Fac. Eng. Nagoya Univ. **7**, 72 (1955).
2) S. Uchiyama, Y. Un-no, Y. Sugiyama and K. Shogenji: Res. Rep. Nagoya Ind. Sci. Res. Inst. 8, 17 (1955) (in Japanese).
3) T. R. Scott: Transistors and Other Crystal Valves (MacDonald and Evans, London, 1955) 95.
4) For instance, H. C. Torrey and C. A. Whitmer: Crystal Rectifiers (McGraw-Hill, New York and London, 1948) 85.
5) V. A. Johnson, R. N. Smith and H. J. Yearian: J. App. Phys. **21**, 283 (1950).
6) J. Bardeen and W. H. Brattain: Phys. Rev. **75**, 231 (1948).

Errata

On Lead Telluride Rectifiers
Y. Sakaki, K. Shogenji, Y. Un-no, S. Uchiyama and Y. Sugiyama
Mem. Fac. Eng. Nagoya Univ. **7** (1955), 72-80.

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