ON LEAD TELLURIDE RECTIFIERS

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The diode characteristics of PbTe are measured. The rectification ratio at room temperature is about 10, and peak voltage is about 2 volts. The effects of contact pressure of the whisker, of flowing current and of temperature are studied. From characteristics of PbTe-PbTe contact the rectifying barrier is considered to be at free surface, as in cases of Ge and PbS. The height of the barrier is estimated to be 0.15 ev. The results are explained by ordinary theories qualitatively, but quantitatively speaking, many contradictions exist between the experimental results and the theories.

I. Introduction

Semiconducting intermetallic compounds such as InSb and GaSb etc. have attracted the attention of many investigators, as well as Si and Ge, since Welker[1] pointed out that the former compounds have an interesting nature and are similar to the latter in several properties. PbS, PbSe and PbTe, which are thought to be ionic or partially ionic crystals, are of interest too, because they are amphoteric, *i.e.* N- or P-type according to the condition of preparing the samples or to their later treatment, and have relatively small energy gap between the conduction band and the full band and hence show transistor action. They have the NaCl type lattice structre, whereas InSb and GaSb have the zincblende structure, Si and Ge the diamond structure. This is the reason why we project systematic investigations of PbS, PbSe and PbTe.

These three materials have similar properties. It was reported by Hogarth[2] that PbTe crystal showed transistor action at 90°K but few rectifying action at room temperature and hence a rectifying barrier was not effective at this temperature, while PbS and PbSe showed transistor action even at room temperature.[3] We can show, however, that PbTe has a pretty rectifying property at room temperature even when it is not so much purified.

After giving some simple accounts of the crystal, we shall describe qualitative features of this rectifier, and then partially quantitative interpretations.

II. Preparation and Properties of Crystals

The PbTe crystals used in this experiment are of P-type and not so much

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purified. Research on the method of purifying the materials and of growing large single crystals is now in progress. The method, employed here as a merely preliminary one, is mentioned briefly below.

Atomic 50% of lead and tellurium are mixed in a fused silica tube crucible, which is then evacuated and sealed. After being heated at about 1000°C for 8 hours in a furnace it is lowered out of the furnace slowly. The chance of getting large single crystals is poor now, but small single crystals, having size enough for rectification measurements, are easily got from the ingot thus obtained. It is desirable to use a double furnace for getting large sigle crystals.[4)]

The crystals obtained by the above method are of P-type, being perhaps due to the oxygen left in the crucible. The crystals melted in the hydrogen atmosphere are of N-type.

The crystals have silvery luster, and are brittle and easily cleft.

The fundamental electrical properties [5)] are also described briefly. The Hall coefficient of the crystal used is a constant independent of temperature within an experimental error. The value is $+2.1\ cm^3$/coulomb throughout measured extrinsic temperature range, *i.e.* between 90°K and 400°K. The temperature coefficient of resistivity at lower temperature is positive, which is expected from the constant Hall coefficient independent of temperature. The resistivity is: 2.5×10^{-3} ohm-cm at room temperature; 2.0×10^{-4} ohm-cm at 100°K.

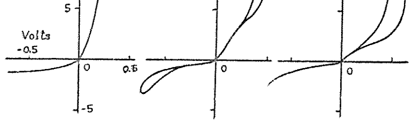
III. General Features

The PbTe specimens used are small single crystals cleft from large ingot by using a razor blade. The surface which the whisker touches is a cleavage plane, and the opposite surface, used as a base, is nickel-plated and soldered to copper plate. The whisker is tungsten wire 0.5 mm in diameter, the end of which is sharpened electrolytically by means of alternating current and NaOH solution. The whisker touches the cleavage plane by means of a feeble spring and its pressure is varied by using a screw.

Current-voltage characteristics are measured under dynamic condition by means of oscilloscope and under static condition by meters.

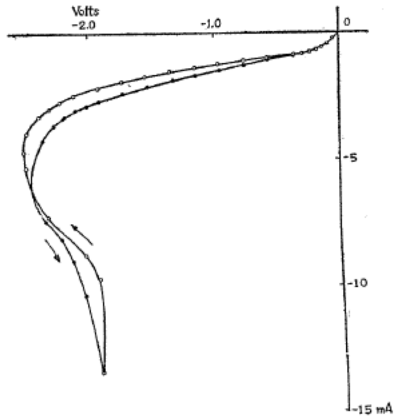
The characteristics obtained show some variety depending on the specimen, the place of contact in specimen, the contact pressure and the previous history of the contact.

Some characteristics are shown in Fig. 1. In some cases hysteresis in both directions and negative resistance in the reverse direction appear under both dynamic and static conditions. Hysteresis loop in the forward direction has a tendency to diminish when contact pressure is increased or after electrical forming is made. Under static condition, reverse curves, showing hysteresis and negative resistance such as shown in Fig. 2, are occasionally obtained. It is remarkable that the portion convex upward in the curve of forward direction sometimes appears as shown in Fig. 1 *b* and *c*. The reason for this is not clear. But, this



(*a*) (*b*) (*c*)

FIG. 1. Examples of dynamic characteristics.



convex part tends to disappear when the pressure of the contact is increased or after comparatively large current passes through the contact.

The characteristic values of the rectifier are listed in Table 1.

FIG. 2. A reverse characteristic.

TABLE 1. The Statistical Vaues of the Rectifiers at Room Temperautre.

	Forward resistance at 0.5 volts (in ohm)	Reverse resistance at 1 volt (in ohm)	Rectification ratio (at 0.5 volts)	Barrier height (in ev.)	Peak back voltage (in volt)
Mode	20	500	5	0.15	2.0
Mean value	140	770	10	0.17	
Standard deviation	130	950	9	0.11	
Max. Value	1000	3300	108	0.63	
Min. Value	4	70		0.02	

Effect of Pressure. Variation of characteristics with the contact pressure of whisker is observed by means of oscillographic method, although the contact pressure is not measured quantitatively.

The contact pressure employed is of the order of 1 g. When the pressure is increased, the resistance of both directions, rectification ratio and peak back voltage become small. If the whisker is over-pressed once, the characteristic is not often recovered to the original when the pressure is released again. Fig. 3 illustrates a typical variation of characteristic with contact pressure.

Generally speaking, a rectifier with low contact pressure has a higher rectification ratio. But at that time its characteristic is often unstable and the resistance of forward direction is rather high. Better characteristic is to be obtained by electrical forming.

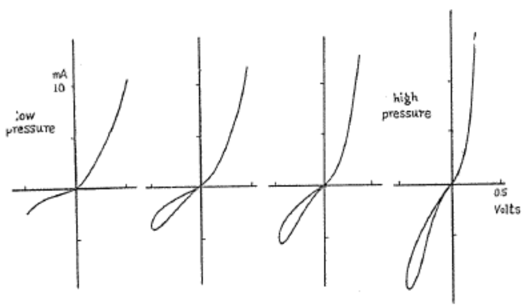


FIG. 3. A variation of characteristic with contact pressure.

Effect of Flowing Current. After a current passes through the contact, a change of characteristic occurs. It is, of course, more noticeable when forward resistance is large and characteristic is unstable, the contact pressure being low. This phenomenon is of importance in connection with electrical forming of rectifiers and transistors.

When the whisker merely touches the specimen slightly, the forward curve sometimes has hysteresis loop and its resistance is rather high. But if a larger current *e.g.* 50 mA once flows in the forward direction, then the resistance decreases and the above hysteresis disappears practically. An over-current in the forward direction decreases the reverse resistance and rectification ratio.

As to the reverse direction, a current flowing for a few minutes, corresponding to a voltage smaller than the peak back voltage, increases the reverse resistance. An over-current in the reverse direction, however, decreases the reverse resistance.

Summing up the results, the forward current decreases the forward resistance and the reverse current increases the reverse resistance, but an over-current in either direction makes the rectifier worse.

From the above informations we may have the way to get good rectifiers. The simplest, way, as far as we attempted, is as follows: the whisker is lowered from above on the specimen until it touches the surface slightly, and this touch is confirmed by observing the oscilloscope which is arranged to display the current-voltage characteristics of rectifier when the whisker comes in contact with the surface; then an alternating current 2 or 3 volts is applied by a voltage regulator to the contact for one second or two. Thus the rectifier whose rectification ratio is comparatively high and characteristic more stable than earlier is got.

Effect of Temperature. In addition to the measurements at room temperature, the characteristics at 100°K are measured using liquid air. The characteristics at this temperature are more stable than those at room temperature. The characteristic values are tabulated in Table 2. The forward resistance is of the same order as that at room temperature. For a larger voltage this is thought to represent the spreading resistance. Therefore the variation of forward resistance is inconsistent with the variation of bulk resistivity with temperature, because the bluk resistivity at liquid air temperature is smaller than that at room temperature by more than one order, while the contact area cannot be expected to vary more than one order though it is not measurable. The similar inconsistency is reported in germanium high back voltage rectifiers.[6]

TABLE 2. The Statistical Values of the Rectifiers at Liquid Air Temperature.

	Forward resistance at 0.5 volts (in ohm)	Reverse resistance at 1 volt (in ohm)	Rectification ratio (at 0.5 volts)	Barrier height (in ev.)	Peak back voltage (in volt)
Mode	75	1500	25	0.17	
Mean value	96	3400	39	0.16	3.6
Standard deviation	47	4000	23	0.06	
Max. Value	208	12500	77	0.28	
Min. Value	48	800	4	0.12	

The reverse resistance becomes higher than that of room temperature, hence rectification ratio is high and peak back voltage also high.

Benzer[6] recognized that in high back voltage germanium rectifiers the reverse current consists of the following three components : (i) saturation component (diode contribution) which results from a fraction of volt ; (ii) linear component (ohmic contribution) which follows the first component; (iii) the third component is one which rises rapidly with voltage. The first two components vary rapidly with temperature. Therefore form of the curve expressing the reverse current varies with temperature. We can also see that the reverse current consists of these components in PbTe. As shown in Figs. 4, 8 and 10 the first component can be seen at room temperature, while it cannot be recognized at 100°K but linear component is clearly seen.

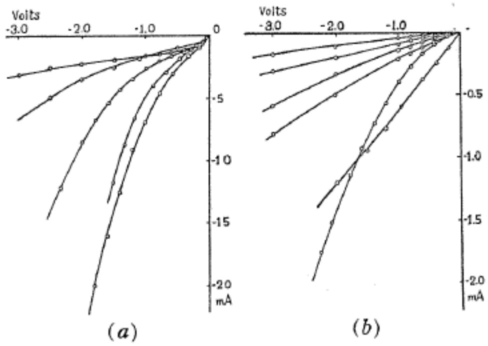


FIG. 4. Reverse characteristics.
(*a*): At room temperature.
(*b*): At liquid air temperature.

PbTe-PbTe Contact. Inter-semiconductor contact, in the cases of Ge[6] and PbS,[7] has such a current-voltage characteristic that in either direction the curves are similar to that of the reverse direction in metal-semiconductor contact. This phenomenon is curious, but is explained by saying that the barrier already exists in the surface of crystal before it comes to contact with the metal. This is an important fact in connection with surface state and surface phenomena such as rectification and transistor action.

PbTe bar is cleft into two specimens and they are made to contact with their edges each other at right angles as shown in Fig. 5. The opposite side of specimen is nickel-plated and soldered to copper as before. The current-voltage characteristics are measured under both dynamic and static conditions.

The static characteristic is shown in Fig. 5. The curve is symmetrical to the origin, and negative resistance and hysteresis are clearly to be seen. The dynamic characteristics and their variation with contact pressure are shown in Figs. 6 and 7. It is curious that a cross-over appears in Fig. 6 *c*, being remarked in metal-PbS[7] contact.

The characteristics are stable and hysteresis for the variation of

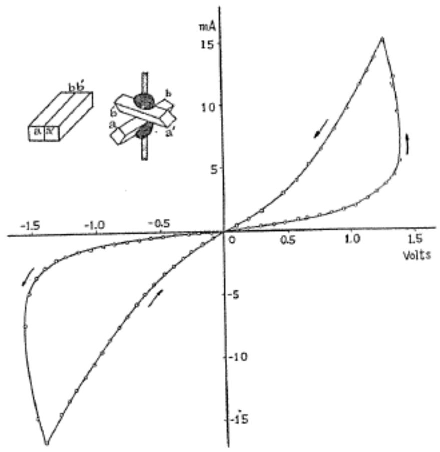
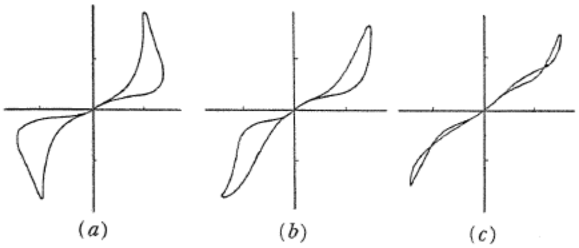
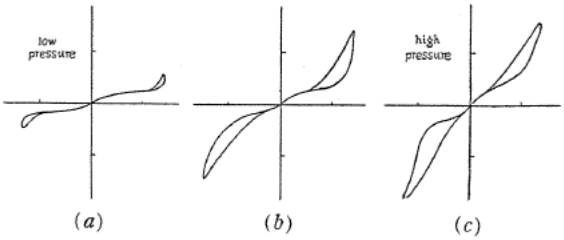


FIG. 5. A characteristic of PbTe-PbTe contact.





the contact pressure is smaller than that of point contact.

From these experiments the barrier is expected to exist at the free surface of PbTe.

FIG. 6 (*upper*). Examples of dynamic characteristic of PbTe-PbTe contact.

FIG. 7 (*lower*). A variation of PbTe-PbTe characteristic with contact pressure.

Effect of Whisker Materials. It is now being surveyed. In a scope of our preliminary works concerning PbTe and PbSe, the results are as follows. As for PbSe, as whisker material varies, the rectification ratio and the height of rectifying barrier are changed, W, Cu, Mo and Ag being the materials used. For PbTe, however, similar effects have not yet been clearly recognized. But this may be the case for PbTe also. Then the fact seems to conflict with the experiment of PbTe-PbTe contact. If, however, surface levels exist in a semiconductor and they are not so many, a barrier exists at the free surface but, after it comes to contact with a metal, the height of the barrier may be affected by the work function of the metal. A careful investigation on these phenomena will be made.

The surface used here is only a cleft one, not polished and not etched. A newly cleft plane seems to be favourable. The plane, cleft and then exposed in the air for several days, occasionally does not show good rectification, being probably due to humidity.

IV. Discussion

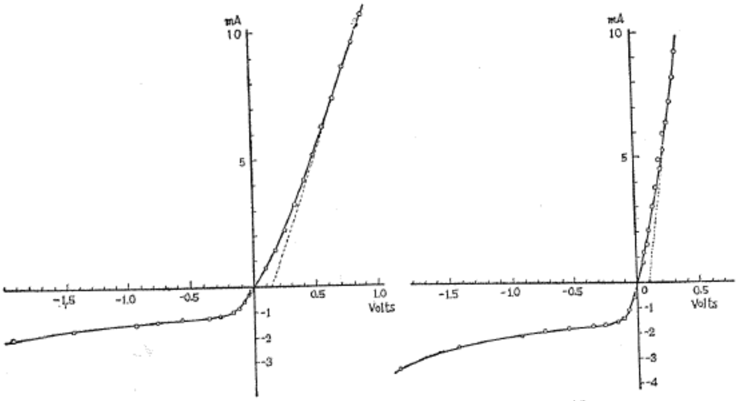
According to the theories of crystal rectifiers the current $I(V)$ through the contact, when the applied voltage is V, is expressed as

$$I(V) = I_S(T)\{\exp(\alpha V) - 1\}, \tag{1}$$

where $I_S(T)$ is the back saturation current and α is to be e/kT, e being electronic charge, k Boltzmann's constant. This formula, in general, accords with experimental results qualitatively but not quantitatively. $I_S(T)$ have different forms according to either the diode theory or the diffusion theory, although both theories are not so different from each other. And whether the diode theory or the diffusion theory should be applied is to be examined for respective cases.

The mean free path estimated from the resistivity and Hall coefficient is of the order of 10^{-6} cm, notwithstanding that the resistivity is due either to acoustical mode of lattice vibration or to optical mode. It is estimated to be 10^{-5} cm at 100°K. On the other hand the thickness of the barrier is got to be of the order of 10^{-6} cm by the ordinary theory with experimental values and properly assumed values. Which theory is to be applied in this case is not clear from the above estimations, but the diode theory seems to be more suitable.

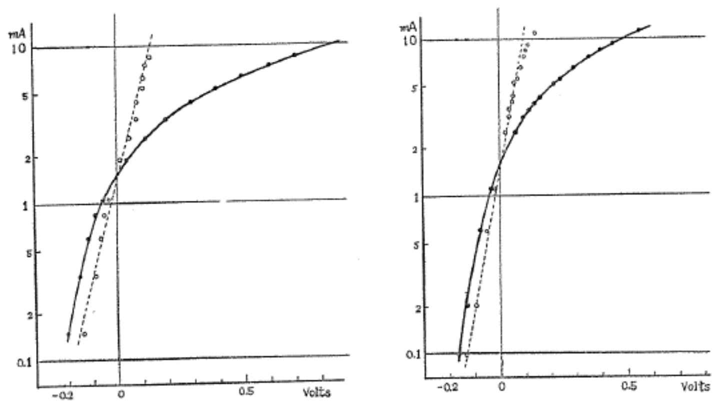
Figs. 8 and 10 show the typical current-voltage characteristics at room temperature and at 100°K, respectively. In Figs. 9 and 11, semi-log plots of the above curves are shown in solid lines. The dotted lines are semi-log plots of $(I+I_S)$ *vs.* $(V-R_S I)$, where R_S is spreading resistance and the resultant voltage is thought to be voltage acting really on the contact. $R_S's$ used are calculated from the slopes of the asymptotes of the forward curves in Figs. 8 and 10, and its values are shown in the figures. $I_S's$ are taken as zero for 100°K and those for room temperature are shown in the figures. These dotted lines are expected to be straight lines from Eq. (1), and their slopes to represent α. The lines are really



(*a*) $R_S \sim 67\ \Omega$. $I_S \sim 1.2$ mA. $V_0 \sim 0.14$ ev.

(*b*) $R_S \sim 23\ \Omega$. $I_S \sim 1.7$ mA. $V_0 \sim 0.09$ ev.

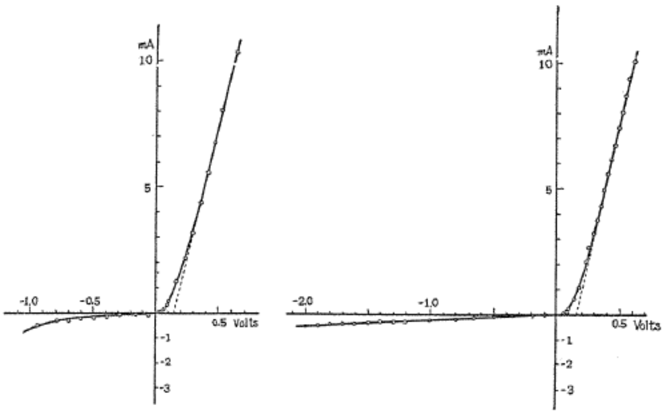
FIG. 8. Characteristics at room temperature.



(*a*) $\alpha \sim 13$

(*b*) $\alpha \sim 18$

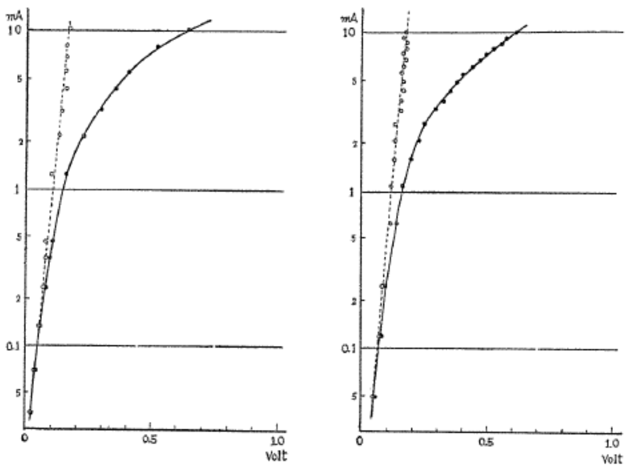
FIG. 9. Semi-log plots of the characteristics at room temperature.



(*a*) $R_S \sim 46\ \Omega$. $V_0 \sim 0.15$

(*b*) $R_S \sim 44\ \Omega$. $V_0 \sim 0.17$

FIG. 10. Characteristics at liquid air temperature.



(*a*) $\alpha \sim 38$

(*b*) $\alpha \sim 42$

FIG. 11. Semi-log plots of the characteristics at liquid air temperature.

straight. The values of α obtained from the slopes are 13 and 18 for room temperature and 38 and 41 in volt^{-1} for 100°K, while they are expected to be 40 and 120 from the theory respectively.

The back saturation current I_S at room temperature is of the order of 1 mA as shown in Fig. 8. Using the above value and the ordinary theories, we get as contact area of the whisker to the semiconductor the order of $10^{-7} \sim 10^{-8}$ cm^2, which is similar whether the diode theory or the diffusion theory is applied. This value is larger than the expected value by one or two orders, while for germanium rectifiers[9] the situation is opposite.

The intersection of the asymptote of the forward curve with the abscissa in Figs. 8 and 10 is to express the height of the rectifying barrier. It becomes about 0.15 ev from the figures. The statistical values of them thus obtained are listed in Tables 1 and 2.

The spreading resistance is given by $R_S = \rho/4r$, where ρ is the resistivity of the semiconductor and r radius of the whisker contact. The temperature dependency of the forward resistance is inconsistent with the temperature variation of the resistivity as mentioned above. If the asymptote of the forward curve represents the spreading resistance, then r should be the order of 10^{-5} cm at room temperature and 10^{-6} cm at 100°K. This is unreasonable. Hence the above cannot be thought to represent the spreading resistance simply. The experimental results, in general, cannot be explained by the ordinary theories quantitatively, as in most cases of semiconductor rectifiers.

Fig. 12 shows the variation of reverse current at the fixed voltage of 0.3 with temperature. If this current may be thought to represent the back saturation current, the slope of this curve gives 0.15 ev as the height of the barrier. This procedure, of course, is very rough, but it may give the order of the value. This value accords with that of the tables approximately.

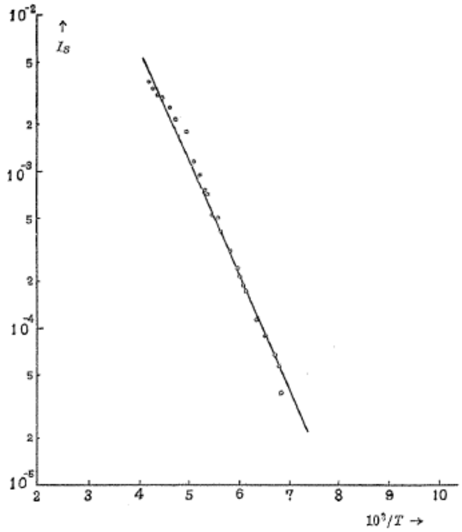


FIG. 12. A variation of reverse current at 0.3 volt with temperature.

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