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## PREPARATION OF LOW CONCENTRATION HIGH MOBILITY *n* AND *p*-PbTe

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**Résumé.** — Nous donnons le résultat de l'utilisation de certaines techniques de croissance et de recuit pour la préparation du PbTe de types *n* et *p*. Il a été possible de préparer du PbTe intrinsèque à la température ordinaire. Des mobilités maximums de  $4,7 \times 10^6$  et  $2,8 \times 10^6$  cm<sup>2</sup> V<sup>-1</sup> sec.<sup>-1</sup> ont été observées dans les matériaux *n* et *p* respectivement.

**Abstract.** — We report the result of some growth and annealing techniques in the preparation of *n* and *p*-PbTe. PbTe has been grown which is intrinsic at room temperature. Maximum mobilities of  $4.7 \times 10^6$  and  $2.8 \times 10^6$  cm<sup>2</sup>/V × sec have been observed in *n* and *p* materials, respectively.

**I. Introduction.** — PbTe is a unique semiconductor in several respects. The low-frequency dielectric constant [1] of the material is exceptionally large ( $\epsilon_0 \approx 400$ ), being about one order of magnitude larger than other typical semiconductors. The exceptional dielectric constant serves to shield out the electric fields of ionized impurities and defects, which leads to mobilities [2] considerably larger than any other semiconductor [3], despite concentrations in the  $10^{17}$ - $10^{18}$ /cm<sup>3</sup> range. These unusual properties have led us to employ PbTe as a useful semiconductor for investigations of helicon-drift current interactions [4, 5] and electron-phonon studies [6, 7]. Since these experiments involved the passage of large current densities (up to  $\sim 10^5$  A/cm<sup>2</sup>) through the samples, it was necessary to obtain high mobility, low concentration PbTe in order to avoid heating of the samples. The results reported in this paper are due to efforts directed principally toward that goal, therefore the present data do not represent a complete study. The purpose of this paper is to report several record values of mobility and concentration and to stimulate further studies.

**II. Experimental methods.** — The samples were cut from boules of Bridgman and boat grown PbTe, and were single crystals with about half oriented and the rest randomly oriented. The samples were cut with a variety of techniques, including spark cutter, jeweler's saw, and diamond wheel. Typical dimensions were  $1 \times 2 \times 10$  mm<sup>3</sup>, although depending on the

use, the dimensions might vary substantially from this. Carrier concentrations were measured by conventional Hall and helicon techniques. The latter had the advantage that no leads were attached to the sample, which sometimes gave spurious results in *p*-type material since it is difficult to make ohmic contact to *p*-PbTe, particularly at cryogenic temperatures. In general, the helicon concentration measurements agreed with the Hall measurements.

Hall mobility was determined by one of three methods of measurement. These were: (1) combining the measurements of Hall constant and resistivity with a 4-probe technique to yield mobility ( $\mu = \sigma/ne$ ), (2) a plot of transverse or longitudinal magnetoresistance,  $\Delta\rho/\rho$ , vs  $B$  shows a change of slope from about 1.8 to 0.5-1.0 at  $\mu B \approx 1$  as the sample goes from the so-called low field to the high field region, (3) helicon transmission structure disappears at  $\mu B = \omega_c \tau \approx 1$ , which permits determination of mobility. All three methods yield consistent values of mobility.

**III. *n*-PbTe.** — *n*-PbTe was treated by vapor and vacuum annealing techniques. Table I illustrates the results of concentration and mobility measurements on a large number of *n*-type samples which were isothermally annealed in an evacuated sealed pyrex ampule (fore pump pressure of  $\sim 1$   $\mu$ ) at 400 °C. The cool-down time of the samples was that of the furnace and was of the order of two hours.

The salient point of table I is that the equilibrium concentration of  $\sim 1.2 \pm 0.2 \times 10^{17}$  electrons/cm<sup>3</sup>

TABLE I  
Results of vacuum annealing at 400 °C *n*-PbTe (4.2 °K)

Sample No.	Before Anneal		Duration of Anneal (hours)	After Anneal	
	Conc. (cm <sup>-3</sup> )	Mobility (cm <sup>2</sup> /V × s)		Conc. (cm <sup>-3</sup> )	Mobility (cm <sup>2</sup> /V × s)
—	—	—	—	—	—
N-17	3.3 × 10 <sup>17</sup>	—	74	1.25 × 10 <sup>17</sup>	—
N-27	6.0	—	74	1.18 × 10 <sup>17</sup>	1,900,000
N-29B	6.2	—	9	1.15	—
N-36	4.8	—	?	1.35	1,600,000
N-44	1.6	1,300,000	672	0.76	3,600,000
N-54	—	—	115	1.43	2,000,000
N-55	2.6	600,000	15.8	1.32	1,500,000
N-57	—	—	15.8	1.07	—
N-61	—	—	?	1.13	1,800,000

is reached in a relatively short time (< 9 hours). (Sample N-44 is somewhat anomalous in that its initial concentration and mobility are respectively lower and higher than normally observed in unannealed crystals.) It was observed that the annealing process increased the unannealed mobility (typically about 700,000 cm<sup>2</sup>/V × s) by about a factor of two or three, with some correlation between longer anneal times and larger mobilities.

These results are somewhat in disagreement with those reported by Scanlon [8] who observes that after annealing *n*-PbTe at 400 °C the concentration is 9 × 10<sup>16</sup>/cm<sup>3</sup> and still decreasing after 59 hours of anneal time.

The largest mobilities were obtained by annealing *n*-PbTe in an evacuated sealed quartz ampule in a vapor of Pb<sub>72</sub>Te<sub>28</sub> with both held at 400 °C over long periods of time. The Pb<sub>72</sub>Te<sub>28</sub> alloy was spatially separated from the sample. Table II summarizes

TABLE II

Results of vapor annealing of *n*-PbTe (N-10) (4.2 °K).

Condition	Concentration (cm <sup>-3</sup> )	Mobility (cm <sup>2</sup> /V × s)
—	—	—
Unannealed	3.56 × 10 <sup>17</sup>	950,000
30 days	1.30 × 10 <sup>17</sup>	2,020,000
60 days	1.53 × 10 <sup>17</sup>	4,700,000

the results obtained on sample N-10. The data indicates that although the concentration had stabilized after thirty days at about 1.4 × 10<sup>17</sup>/cm<sup>3</sup>, the mobility continued to increase reaching 4,700,000 cm<sup>2</sup>/V × s after 60 days anneal time. It is believed that this is a largest mobility reported for *n*-PbTe. Accidental destruction of the sample prevented a longer

anneal to determine whether or not the mobility could be further improved.

It appears that the way to obtain high mobility *n*-PbTe crystals is by long anneal times either in the presence of a vapor or in a vacuum, rather than by improving crystal growth techniques. This is consistent with known phase relations in the PbTe system. Further study should be made to determine the effect of annealing temperature and time on mobility and concentration in *n*-PbTe.

IV. *p*-PbTe. — Although *p*-PbTe is the most prevalent form in the asgrown material, we have done relatively little work with this type because of the extreme difficulty [9] in making ohmic contacts to *p*-type materials at cryogenic temperatures. However, we report some new results on *p*-PbTe which we observed to be intrinsic at room temperature. This was deduced from the fact that the Hall sign and thermoelectric probe readings at room temperature indicated *n*-type material. Upon cooling to nitrogen temperatures and below the sign reversed and the material became *p*-type, which is indicative of intrinsic material. Although the electrons are the minority carrier at room temperature, their larger mobility ( $\mu_e \simeq 1800$  cm<sup>2</sup>/V × s, vs  $\mu_p \simeq 900$  cm<sup>2</sup>/V × s) gives rise to a manifestation of electron-like properties rather than hole like properties in the intrinsic material.

The helium temperature properties of three such samples of *p*-PbTe are summarized in table III. It is seen that their concentration lies between 0.75 and 1.0 × 10<sup>17</sup> holes/cm<sup>3</sup> and their mobility (up to 2,800,000 cm<sup>2</sup>/V × s) is exceptionally large for *p*-type PbTe. No lower hole concentrations or higher hole mobilities were found in the literature.

There is a principle difference between these samples

TABLE III  
Vapor grown *p*-PbTe (4 °K).  
Hole

Sample	Concentration	Mobility
N-47	$1.0 \times 10^{17}/\text{cm}^3$	$2,000,000 \text{ cm}^2/\text{V} \times \text{s}$
N-48	$0.84 \times 10^{17}$	1,000,000
P-6	$0.75 \times 10^{17}$	2,800,000

and those of the *n*-type PbTe in that these were not annealed but represent material which had been grown by a vapor transfer method which is described below.

High purity (99.9999 %) Cominco Pb and Te in stoichiometric proportions, totaling about 200 g, were cleaned and placed in a cleaned quartz vial about 18 cm long, which was sealed under high ( $10^{-8}$  torr) vacuum conditions. The vial was hung vertically in an electric furnace with the source material at 948 °C and the top of the vial at 844 °C. The system was kept under these conditions for fourteen days during which time approximately one third of the source material was deposited in the top of the vial by vapor transport as a single PbTe crystal. The temperature of the furnace was then lowered to 400 °C and the material removed. As indicated above the material appeared to be *n*-type at room temperature, but subsequent measurements showed that it was *p*-type at cryogenic temperatures.

**V. Conclusions.** — We have shown that high mobility, low concentration *n*-PbTe may be obtained by both vapor and vacuum annealing techniques. Exceptionally low concentration, high mobility *p*-PbTe, which is intrinsic at room temperature, has been grown by a vapor transfer method. It is believed that record high mobilities for *n* and *p*-PbTe are reported here as well as the lowest *p*-concentration material. These results do not support Kobayashi et al [10] conclusion that there is an intrinsic maximum in mobility in *n* and

*p*-PbTe related to the carrier concentration. Selected samples of our *n* and *p* samples lie much above and to the left of the mobility vs concentration curves shown in figure 1 and 2 of ref. 10. It is felt that the maximum in the curves [10] are probably related to the method of preparation of the samples rather than an intrinsic property of the material.

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**Note Added in Proof.** — The highest *n*-type mobilities observed have been obtained recently in a sample of *n*-PbTe which was vacuum annealed for one week at 450 °C. The results for concentration and mobility at 4.2 °K are  $n = 9.3 \times 10^{16}/\text{cm}^3$  and  $\mu = 5,700,000 \text{ cm}^2/\text{V-sec}$ .

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