AIP | Journal of Applied Physics

A Method of Growing Single Crystals of Lead Telluride and Lead Selenide

W. D. Lawson

Citation: J. Appl. Phys. **22**, 1444 (1951); doi: 10.1063/1.1699890
View online: http://dx.doi.org/10.1063/1.1699890
View Table of Contents: http://jap.aip.org/resource/1/JAPIAU/v22/i12
Published by the American Institute of Physics.

A Method of Growing Single Crystals of Lead Telluride and Lead Selenide

W. D. LAWSON
Telecommunications Research Establishment, Malvern (Ministry of Supply), England
(Received May 31, 1951)

Single crystals of lead telluride measuring up to $1\frac{1}{4}$-cm diameter and 6 cm long have been grown in sealed silica crucibles by the Bridgman-Stockbarger method of lowering a melt slowly through a freezing level. The crystals have been grown for the purpose of testing the semiconducting and allied properties of lead telluride in that form. Extreme purity of the materials and cleanliness of the crucible have been found essential for successful growth. X-ray tests have shown that the specimens are single crystals. The purest crystal grown so far had a conductivity corresponding to an electron concentration of 5×10^{14} per cc. Attempts to introduce excess of one of the constituents—lead or tellurium into the crystal lattice during growth have not so far been successful.

1. INTRODUCTION

IT is necessary, in order to understand the fundamental electronic behavior of semiconductors like PbTe, to make measurements over a wide range of temperature of such electrical properties as conductivity and Hall constant. It is possible to make the measurements, as indeed has often been done, on evaporated layers, compressed powder slabs, or polycrystalline ingots, but the values of conductivity so obtained are bound to be affected to some extent, particularly at lower temperatures, by the intergranular boundaries present in such specimens. The best way of overcoming this difficulty is by making measurements on specimens which have no such boundaries, i.e., on single crystals, and it is for this purpose that the crystals have been grown.

A crystal size of 4 cm, by 1 cm, by 1 mm was initially required for the electrical experiments so this size was set as the target to be achieved in growing the crystals.

2. METHOD OF GROWING THE CRYSTALS

A study of the various ways of growing single crystals—by evaporation, from solution, etc., led to the conclusion that the method of growing from a melt offered most hope of yielding crystals of the size required. Even after this decision had been made there was still a considerable choice of experimental technique of growing crystals from a melt. After some initial experiments the double-furnace method, which has been used with considerable success in recent years by Stockbarger[1] and others[2] for growing crystals of optical materials, was selected because it gives best control of the growing conditions and is therefore most likely to give consistent results. In this method the material is melted in an upper furnace, in a crucible with a conical bottom, and lowered slowly into a lower furnace whose temperature is below the melting point. At some intermediate level there exists a freezing plane at which the molten material solidifies, and if conditions are right a single crystal grows.

FIG. 1. Silica crucible.

Stockbarger puts the main essentials for successful growth of pure single crystals in this way as follows: (i) Dropping rate and temperature gradient such that isothermals around the freezing level are horizontal. This condition ensures that cooling is from the bottom and not from the sides, and prevents random crystal growth inward from the sides.

(ii) Sharp temperature gradient around the freezing level. This produces a high flow of heat through the freezing surface and enhances rejection of impurities by vigorous bombardment of the freezing level.

3. SPECIAL PROBLEMS WITH LEAD TELLURIDE

The melting point of PbTe is 904°C so the temperatures within the top and bottom furnaces should be in the region of 950°C and 850°C, respectively. The difficulties associated with heating PbTe to 950° are as follows:

(i) PbTe cannot be heated in air as it oxidizes readily. It must therefore be heated in an inert atmosphere or in vacuo.

(ii) At 950°C the vapor pressure of lead telluride is fairly high (several cm Hg) so there is considerable loss of material if it is heated at that temperature for any length of time in an open crucible. There is also a certain amount of dissociation into free lead and tellurium, and since, at 950°C, the vapor pressure of

[1] D. C. Stockbarger, Rev. Sci. Instr. 7, 133, 1936.
[2] Tuttle and Egli, J. Chem. Phys. 14, 571, 1946.

tellurium is considerably higher—the order of 100 times—than that of lead, the material left after free evaporation from an open crucible will have a stoichiometric excess of lead. Thus if it is required to retain the initial proportions of Pb and Te the crystal must be grown in a sealed crucible.

(iii) At 950°C lead telluride and the dissociated elements are fairly active chemically so the crucible material has to be chosen with some care. Fused silica does not react with lead telluride in the absence of oxygen, so the crystals have been grown in sealed crucibles of this material.

4. PREPARATION OF THE MATERIALS

It is well known that extreme purity of the materials is essential both for growing good single crystals and for obtaining reliable results from the electrical experiments. It is thus essential firstly to start with high grade materials of guaranteed purity and secondly to take all necessary precautions to prevent contamination during handling and growth. The ordinary commercial grades of chemically pure material do not achieve anything like the standard of purity required but spectrographically standardized grades of both lead and tellurium with a total impurity content better than 1 in 10^5 have been obtained and used as the starting material. It is necessary to remove the oxide coat with which these are covered when received. This can be done with lead by heating it to 700°C in an alumina boat in a stream of hydrogen. Tellurium cannot be treated this way as there is a tendency for hydrogen telluride to be formed, so the oxide is separated by distillation in a pyrex glass tube at a residual pressure of 10^{-6} mm Hg. Before distilling the tellurium the tube and pumping system are flushed several times with argon.

A crucible of the shape shown in Fig. 1 is formed from clear fused silica tube of about 1-cm bore. The shape of the cone at the bottom has not been found to be critical in any way. The transparent variety of silica is used in preference to the translucent variety as there is some danger of contamination from the latter by the emission, at high temperature, of gas from the small bubbles which are the cause of its translucency. The crucible is cleaned before use by boiling with nitric and chromic acids and flushing several times and then boiling with distilled water. It is then connected to a vacuum system, pumped out, and outgased at about 600°C.

The lead and tellurium, in the required proportions, are then put in, and the crucible sealed back on to the pumping system. It is left on the system at a pressure of 10^{-6} mm Hg for about two days before it is sealed off at the constriction. This long period of pumping out is necessary to ensure that as much occluded air as possible is removed from the mixture. It is not possible to heat the mixture above about 100°C to help in expelling this air as further heating merely assists the

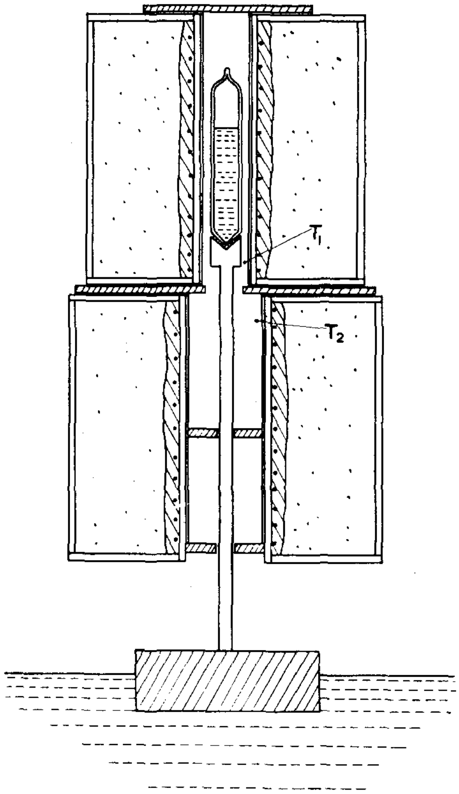

FIG. 2. Crystal growing apparatus.

formation of an oxide and causes evaporation of tellurium.

Combination of the lead and tellurium is effected at this stage, after sealing off, by heating the crucible and contents in a Bunsen flame. The reaction is exothermic and a flash of redness along the mixture indicates the formation of lead telluride.

5. GROWTH OF CRYSTAL

The crucible is then transferred to the crystal growing apparatus which is illustrated in Fig. 2. The two furnaces are made as separate units and mounted vertically one on top of the other as shown, on a stand above a trough of water. The crucible is cemented to the nickel supporting rod which rests on a float on the water, and the level of the water is adjusted until the crucible is entirely within the top furnace. The crucible can be lowered at the appropriate time by letting water run out of the tank. The furnace tubes are lined with nickel tubes which serve the double purpose of eliminating temperature gradients within the separate furnaces and protecting the refractory furnace tubes in the event of explosions. Any gaps at the furnace junction and top cap are sealed with alumina cement to exclude draughts.

The furnaces are then switched on and the power supply increased gradually until the upper and lower temperatures of 950°C and 850°C, respectively, are reached. The temperatures are measured bychromel-alumel thermocouples T_1 and T_2 placed one inch on either side of the insulating baffle. The power supply is controlled by Sunvic Energy Regulators which give enough control to keep the temperature well within 10°C of the nominal values. This degree of stabilization is adequate for the lowering rates used, particularly in view of the high thermal inertia of the furnaces.

The apparatus is left in this condition, with the contents of the crucible molten, for about 12 hours. This prolonged melting is necessary for the following reasons: first, it insures that the lead telluride is completely molten so that no small seeds of solid material remain; second, it allows thorough mixing and reaction of the elements so that the composition of the compound is uniform throughout the melt, and finally it permits diffusion of insoluble impurities to either top or bottom of the melt leaving the middle relatively purer. The crucible is then lowered at any desired rate by siphoning water out of the trough through a glass tube fitted with a stopcock. This gives control of the lowering speed between 2 mm/hr and 2 cm/hr as desired. The lowering method has the great advantages of simplicity and almost complete freedom from breakdown of any kind, provided the stopcock is thoroughly clean. The lowering speed diminishes very slowly as the water level falls but this has not been found to be any disadvantage and could, if necessary, be almost completely eliminated by using a long siphon tube so that the head of water remains practically constant. It has been found necessary, with the above temperature difference, to use a lowering speed less than 1 cm/hr to insure single crystal growth.

When the crucible is lowered completely into the bottom furnace it is cooled to room temperature over a period of about 24 hours. More rapid cooling sets up strains in the crystal which leave it weak and fragile so that it breaks up very easily.

Usually, if no oxide of either element is present, the crystal slips easily and cleanly out of the crucible. If however one or more of the oxides of lead or tellurium are present, either through inadequate pumping out, or incomplete deoxidizing, these react with silica to form a kind of glass which glues the crystal very effectively to the crucible. When this happens it is almost impossible to extract the crystal whole and sometimes shattering of the crucible during cooling is caused by differential contraction.

6. EXPERIMENTAL RESULTS

Single crystals measuring up to $1\frac{1}{4}$ cm diameter by 6 cm long have been grown using this technique and there is no apparent reason why larger ones could not be grown if required. The crystals, which have a face-centered cubic NaCl type structure, are opaque and have a metallic, almost silvery, appearance. They are brittle and cleave quite readily parallel to (100) planes when tapped with a razor blade. Cleavage in other planes is difficult, though not impossible, to produce.

The purest crystal so far grown had an electrical conductivity corresponding to an electron concentration of 5×10^{14} per cc and has been shown to be an intrinsic semiconductor down to 200°K. The conductivity and Hall constant measurements which lead to this conclusion are being published elsewhere.

Tests in an x-ray goniometer have indicated as follows that the specimens are in fact single crystals. Rectangular slabs with faces parallel to (100) crystal planes were cleaved from the ingots and the angles between their faces measured. It was found that, within the accuracy of the measurement, opposite faces were parallel to each other and perpendicular to adjacent faces. The individual faces were also examined, section by section, with a narrow x-ray beam 0.4 mm wide, and found to be plane. Owing to the very high absorption of x-rays in lead telluride (absorption coefficient $\doteqdot 250$ for the x-rays used) it is only the surface layers which are being examined and not the bulk crystal, but the evidence is nevertheless fairly conclusive that the slabs are single crystals.

Specimens have also been tested by x-rays for traces of free lead or tellurium but none have been found.*

In order to test the effect of an excess of one of the constituents lead or tellurium on semiconducting properties, an attempt was made to grow a number of crystals ranging in composition from 2 percent excess Pb to 2 percent excess Te. The appropriate excess was introduced into the initial mixture and the crystal growing experiment carried out in the usual way. Examination of the resulting crystal revealed however that the excess had not been absorbed by the crystal lattice but had been forced to the top during the growing process, and the crystal underneath retained an approximately stoichiometric composition. This was most noticeable when a large excess of lead had been added, as the top of the resulting crystal was then tough and could not be cleaved and was obviously almost entirely composed of lead. Varying the growing conditions has not so far made any appreciable difference to this result.

Experiments are continuing in an endeavor to produce purer crystals and to introduce excess of the individual constituents into the crystal lattice.

7. LEAD SELENIDE

A single crystal of lead selenide has been grown recently in the same way, in a silica crucible. The melting point of this compound is 1065° so furnace temperatures of 1110°C and 1010°C were used in conjunction with a lowering rate of nearly 1 cm/sec. The selenide has a crystal structure and cleavage properties similar to the telluride, but is darker and

* This test was carried out by K. Lark-Horovitz of Purdue University.

less silvery in appearance. Its electrical properties are being measured.

ACKNOWLEDGMENTS

The author wishes to thank Mr. G. E. Bacon of A.E.R.E., Harwell, Berkshire, for carrying out x-ray measurements to determine the form of the crystals. The work described in this paper was carried out at the Telecommunications Research Establishment, Malvern, England, as part of the research program of the British Ministry of Supply, and is published by permission of the Chief Scientist, British Ministry of Supply.

JOURNAL OF APPLIED PHYSICS VOLUME 22, NUMBER 12 DECEMBER, 1951

General Theory of Electromagnetic Horns*

A. F. STEVENSON
Department of Mathematics, Faculty of Science, Farouk I University, Alexandria, Egypt†
(Received June 8, 1951)

Exact equations for the propagation of electromagnetic waves in a perfectly conducting horn of arbitrary shape are given. They take the form of an infinite set of simultaneous ordinary linear differential equations, and can be interpreted as the equations of propagation of a system of coupled E- and H-waves. If the coupling is neglected, we need only consider a single differential equation for each E- and H-wave, which can be solved approximately by the W.K.B. method. This approximate solution brings out the distinction between "transmission regions" and "attenuation regions" of the horn, as found by Barrow and Chu for the sectoral horn.

It is shown that the error due to neglect of coupling is, in general, of the order of the square of the flare angle as far as the variation of the field along the horn is concerned, but is of the first order in the flare angle as regards the variation of the field over the cross section. The coupling cannot, however, be neglected between modes of propagation which have the same cut-off frequency for all cross sections. The propagation characteristics of several special shapes of horn are discussed in detail.

1. INTRODUCTION

THE theory of the propagation of electromagnetic waves in a perfectly conducting sectoral horn has been given by Barrow and Chu.[1] Exact solutions for a conical horn are also available.[2] But no attempt appears to have been made to give a general theory applicable to horns of any shape.[3] It is the purpose of this paper to give such a general theory.

In Sec. 2, exact equations for the propagation of electromagnetic waves of a single frequency in a perfectly conducting horn of arbitrary shape are given—a "horn" being defined as a surface such that any plane perpendicular to a given line meets this surface in a single closed curve. The equations take the form of an infinite set of simultaneous ordinary linear differential equations in an infinite number of unknowns, the coefficients occuring in the equations being known when the eigenfunctions and eigenvalues which occur in wave-guide theory are known for all sections of the horn. These differential equations can be regarded as giving rise to a system of coupled E- and H-waves.

In Sec. 3, the case of horns of small flare is considered, the coupling between different modes of propagation being neglected, so that we have to deal with a single ordinary differential equation. An approximate explicit solution of this equation can be given for what is here termed the "normal case." This approximate solution brings out the distinction between "transmission regions" and "attenuation regions" of the horn, as found by Barrow and Chu[1] for the sectoral horn, and approximate expressions for the phase velocity (in the transmission region) and the attenuation constant are given.

In Sec. 4, the validity of the neglect of coupling is investigated. It is shown that, as far as the variation of the field components along the horn is concerned, the error committed by neglecting coupling is of the second order in the flare angle, provided that the modes concerned do not have the same cut-off frequency for all cross sections; but that the error is of the first order in the flare angle as regards the variation of the field over a cross section. The coupling cannot be neglected between modes having the same cut-off frequency.

In Sec. 5 expressions for the field components correct to the first order in the flare angle are given for the normal case, and the problem of calculating the field *outside* the horn is discussed briefly. In Sec. 6 various special horns are considered in detail, and some general

* A preliminary account of this paper was given at the American Mathematical Society's Symposium on Electromagnetic Theory held at Cambridge, Massachusetts, in July, 1948.
† Now at Bishop's University, Lennoxville, Quebec, Canada.
[1] W. L. Barrow and L. J. Chu, Proc. Inst. Radio Engrs. **27**, 51 (1939).
[2] See, for instance, S. A. Schelkunoff, *Electromagnetic Waves* (D. Van Nostrand Company, Inc., New York, 1943), pp. 399–404.
[3] The case of horns of small flare is referred to briefly by Schelkunoff (pp. 405, 406 of reference 2). The equations there suggested, however, do not appear to be correct, even as approximate equations for what is termed the "normal case" in this paper (the terms involving U_{nn}, X_{nn} in our Eqs. (3.1), (3.2) appear to be omitted).