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Gray Tin Single Crystals*

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A method of growing gray tin single crystals from a liquid amalgam is presented together with a description of the apparatus and specification of the conditions of growth. Photographs of typical crystals ranging in size up to 2 cm and showing well-developed crystallographic planes are included. Residual resistance measurements indicate a total impurity content of the order of 0.001%. The energy gap is the same as for transformed material but the low-temperature mobilities are considerably higher. Evidence that the gray-to-white transformation is of the diffusionless type is presented.

INTRODUCTION

SINCE the discovery in 1950 that gray tin is a semiconductor,[1] the problem of obtaining specimens in other than powder form has received the attention of a number of investigators. As a result considerable progress has been made in producing coherent samples by various techniques including compressing the powder into compact rods[2] and transforming fine wires,[3] thin foils,[4] and tin amalgams.[5] The study of these coherent specimens has made possible more direct and reliable evaluation of the semiconductor parameters which had been determined in the earlier work and also the extension of this to certain measurements which could not be made on powder samples.[6] Yet because all of these techniques involved the transformation from one solid phase to another, the product lacked the high degree of crystalline perfection required for the investigation of many interesting semiconductor properties and our knowledge about gray tin remains quite incomplete. This is especially true of the optical properties but also of all properties to the extent that they may be anisotropic and they may be sensitive to lattice imperfections.

There have been numerous attempts by several investigators to deposite tin atoms directly in the gray tin structure.[2,7] Electrolytic, chemical, and vapor deposition techniques have been tried under a wide range of conditions and using various substances as substrates. These as well as a previous attempt to grow crystals from mercury solution[2] were unsuccessful. Nevertheless a reinvestigation of the latter method was undertaken because of a chance observation made while repeating the experiments of Groen[5] on the transformation of tin amalgams. It was noted that if, after

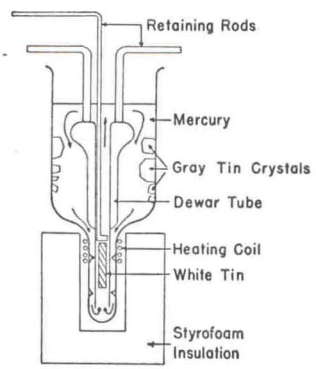

FIG. 1. Crystal growing apparatus

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[1] Busch, Wieland, and Zoller, Helv. Phys. Acta **23**, 528 (1950); A. I. Blum and N. A. Goryunova, Doklady Akad. Nauk S.S.S.R. **75** (No. 3), 367 (1950); J. T. Kendall, Proc. Phys. Soc. (London) **B63**, 821 (1950).
[2] J. T. Kendall, Phil. Mag. **45**, 141 (1954).
[3] A. W. Ewald and E. E. Kohnke, Phys. Rev. **97**, 607 (1955).
[4] J. H. Becker, Phys. Rev. **98**, 1192(A) (1955).
[5] L. J. Groen, Nature **174**, 836 (1954).
[6] A. N. Goland and A. W. Ewald, Phys. Rev. **104**, 948 (1956).
[7] See, for example, L. J. Groen, Koninkl. Ned. Akad. Wetenschap. Proc. **B57**, 122 (1954) and J. H. Becker, Natl. Bur. Standards Rept. 4576 (1956) (unpublished).

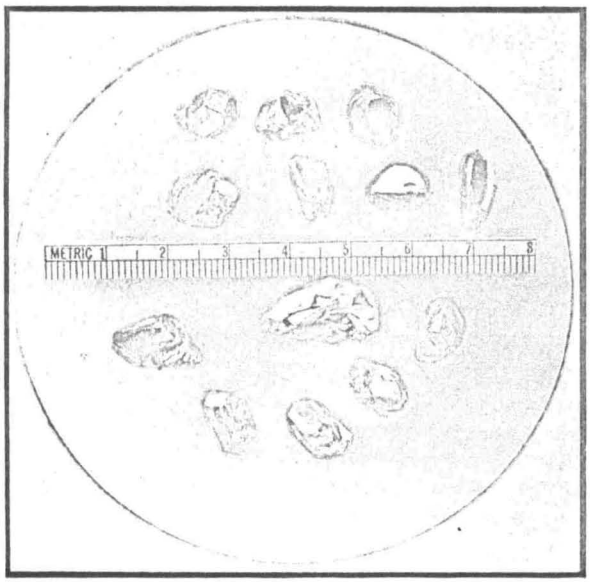

FIG. 2. Gray tin crystals typical of the largest crystals that have been grown.

the transformation to the gray phase, an amalgam containing a few percent mercury was maintained at reduced temperature the mercury was expelled forming droplets on the surface. This indicated a low solubility of mercury in gray tin and therefore that crystals, if they could be grown, would be quite free of mercury.

CRYSTAL GROWTH

The crystal growing apparatus was designed to permit continuous crystallization from a mercury solution locally supersaturated by cooling to $-30°C$, while the tin concentration was maintained by continuous dissolution of the metal in a warmer portion of the mercury. The original design has been modified repeatedly in an effort to concentrate the growth on a small number of crystals beneath the mercury surface. The apparatus being used at present is shown in Fig. 1. This apparatus is placed in a refrigerator at $-55°C$. The charge of tin and surrounding mercury in the lower constricted part of the beaker are maintained at $-20°C$ by means of the heating coil. As tin dissolves a density gradient is established which causes convection and the liquid amalgam rises at nearly constant temperature in the Dewar-type tube. As the solution flows radially outward at the top and downward along the walls it is cooled to a minimum temperature of about $-30°C$. In this particular apparatus crystal growth occurs only at the vertical walls beneath the mercury surface. Tin is supplied to the apparatus in the form of rods 4 mm in diameter and 2.5-cm long at 24 hour intervals.

Intentional seeding with gray tin powder is unnecessary. The initial crystallization product consists of hexagonal plates, presumably the compound $HgSn_{12}$.[8] If, after a week's growth these crystals are removed, further crystallization invariably produces a great number of gray tin crystallites. By removing these repeatedly at one week intervals the number of nuclei is sufficiently reduced to permit reasonably rapid growth of the individual crystals. This growth rate is such that crystals of the size shown in Fig. 2 are grown in a period of a month.

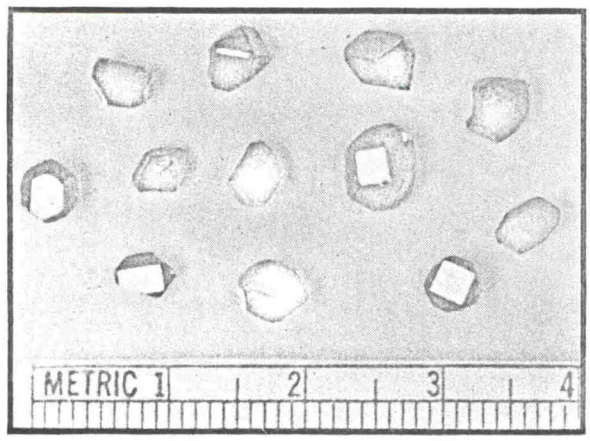

FIG. 3. Gray tin crystals selected and oriented to show external perfection.

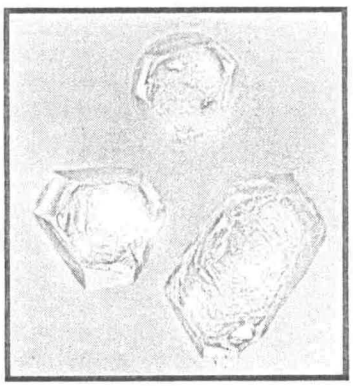

FIG. 4. Crystals oriented to show ring structure of imperfect faces.

CRYSTAL PROPERTIES

The crystals shown in Fig. 2 are the largest that have been grown thus far. The present limitation on the size is that imposed by the dimensions of the apparatus. Though there is no inherent limitation on size, the larger crystals tend to be less perfect as may be seen by comparison with Fig. 3 which shows somewhat smaller crystals selected and oriented to display the external symmetry. Most crystals, regardless of size, have one imperfect face characterized by the ring structure shown in Fig. 4.

Gray tin is brittle and the crystals are readily fractured to expose surfaces of high luster and having the general appearance of broken germanium. This is in

[8] See, for example, M. Hansen, *Aufbau der Zweistofflegierungen* (Julius Springer, Berlin, 1936), p. 809. These hexagonal crystals will always be produced if the minimum mercury temperature is raised to $-10°C$.

contrast with the dull appearance of surfaces exposed when transformed tin is broken. The internal structure of single crystals has also been investigated by means of x-rays. Figure 5 is a reflection Laue pattern of a crystal in the [100] orientation.

When a crystal is cut to prepare samples, internal imperfections in the form of small pockets of occluded mercury are exposed. The number of these is not so great but that they can be eliminated through proper cutting. If this is done the specimens show a remarkable freedom from mercury contamination as is evidenced by residual resistance measurements made on samples transformed to the metallic phase. Attributing the entire residual resistance to the presence of mercury, the indicated mercury content of one of the early crystals was found to be 0.001 atomic percent. This was a *p*-type crystal. More recently, through better control of growing conditions and purification of the mercury, *n*-type crystals of higher purity have been grown.

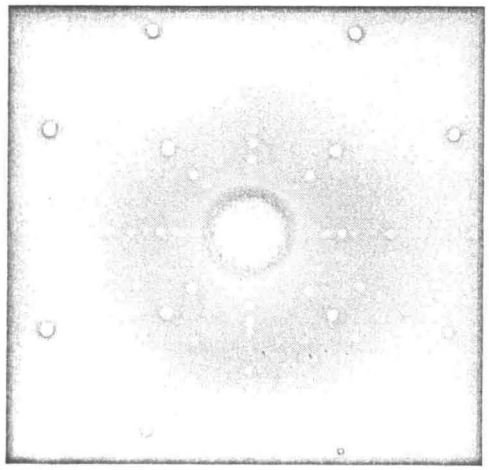

FIG. 5. Reflection Laue pattern of a gray tin crystal in the 100 orientation.

Mercury-free specimens cut from grown crystals and maintained at room temperature usually transform to the metallic phase within a few hours. However a few specimens have remained in the gray phase at this temperature for several weeks. The stability of the crystals at temperatures above 0°C is greatly reduced by contact with mercury. Mercury adhering to the crystal surfaces suddenly goes into solid solution as the temperature reaches about 1°C. At the same time the color changes from gray to white and the crystals become soft as in the normal phase transformation. If only a limited quantity of mercury is present, the crystals are only partially transformed. Specifically if a droplet of mercury is placed on a clean crystal surface a volume of the crystal comparable to that of the droplet is converted. The boundaries of the transformed portion coincide with principal planes of the gray tin lattice delineating an area having the symmetry of the crystal facet on which it occurs as shown in Fig. 6.

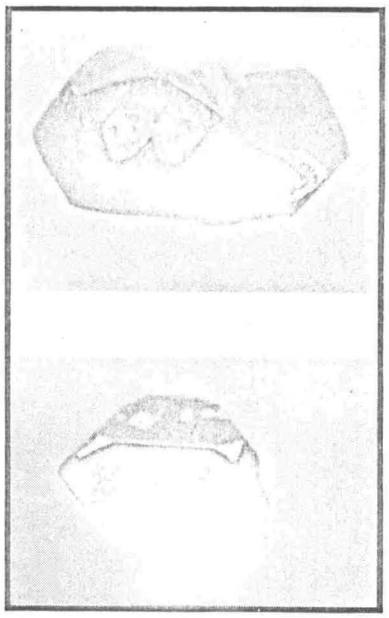

FIG. 6. Partially transformed crystals. The transformation was accompanied by diffusion of mercury into the crystal. Plane boundaries of the transformed regions indicate that the transformation occurs without diffusion of tin atoms.

Plane boundaries such as these generally characterize a diffusionless transformation. In the present case one may conclude that the transformation of pure gray tin to tin amalgam takes place without diffusion of tin atoms.

One of the characteristic features of a diffusionless transformation, namely a stepwise motion of the interface separating the two phases, has been noted in the transformation of pure gray tin to pure white tin. This observation was made on a cleaved surface entirely free of mercury. Under the microscope (150× magnification) one observes the transformation of distinct domains each of which is bounded by the original interface and an arc-shaped curve on the advancing side of the interface. The transformation of an individual domain is completed in a time that is short in comparison with the time interval between domain transformations. The availability of gray tin single crystals should greatly facilitate further investigations of the gray-to-white transformation which, in the past, has been studied much less extensively than the reverse transformation.[9]

An investigation of the semiconducting properties of these crystals is now in progress. Preliminary results on an *n*-type crystal yield an energy gap of 0.08 ev in agreement with the value for transformed tin. At liquid nitrogen temperature both the conductivity and Hall coefficient of this crystal are greater than the values for pure transformed tin indicating a higher electron mobility. This is confirmed by the value of the magnetoresistance coefficient which is also greater for the single crystal.

[9] A study of the gray-to-white transformation of granuals has recently been reported by Burgers and Groen, Discussions Faraday Soc. **23**, 183 (1957). See also E. Cohn and A. K. W. A. van Lieshout, Z. physik. Chem. (Leipzig) **A173**, 1 (1935) which also contains references to earlier work.