GROWTH OF HIGH PURITY SINGLE CRYSTALS OF ARSENIC

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Large, high quality, single crystals of arsenic have been grown from the melt in a high pressure bomb made from synthetic quartz. The crystals have residual resistance ratios (RRR) of up to 5500, the largest reported to date.

1. Introduction

Arsenic, together with its sister elements Bi and Sb belongs to the group V semimetals. This important class of solids is characterized by a small free carrier concentration which is responsible for many interesting phenomena, some of them, in fact, first discovered in these materials. In comparison to Bi and Sb, the study of arsenic has been hindered by a rather severe shortage of high quality crystals because of difficulties associated with the growth of large single crystals. Since arsenic sublimes before it melts, it is necessary to prepare crystals from the vapor phase or grow them from the melt under high pressure (melting point 813°C at about 30 atm). It has been shown [1–5] that both techniques can be used to prepare large single crystals. To learn about intrinsic properties of arsenic, it is essential that the purity of crystals be as high as possible. The spectrographic determination of impurities at the sub-ppm level is difficult and mostly only qualitative. Ultimately, therefore, the best criterion of sample purity and quality is usually the residual ratio, $RRR = R_{300K}/R_{4.2K}$. So far, all measurements reported in the literature have been made on arsenic samples with RRR less than 1000.

In this report we describe an improved version of one of the variants of the growth of arsenic crystals from the melt which we used to prepare large samples of record-high resistivity ratio, typically of 3500–5500. Such ultrapure crystals were required for studies of transport properties currently in progress.

2. Crystal growth technique

The essence of the technique was outlined by Weisberg and Celmer [1] and also by Ketterson and Eckstein [3]. It relies on the Bridgman method of crystal growth using a heavy wall container (bomb) capable of withstanding pressures up to about 40 atm. We have adopted this technique but made several refinements which, we believe, lead to a much higher purity of the resulting crystals.
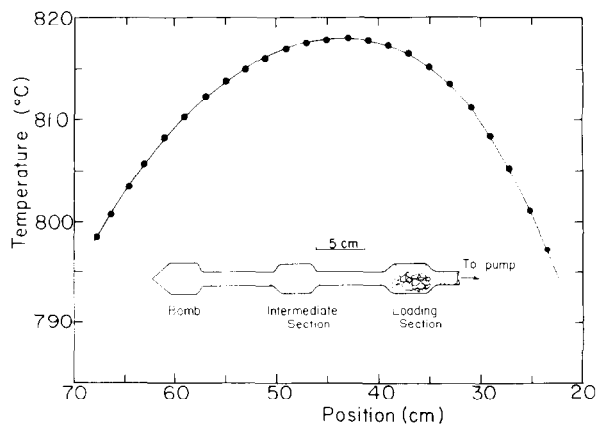

Fig. 1. Temperature profile of the furnace used for the growth of single crystals of arsenic. Schematic diagram of the quartz container is shown in the inset.

The process consists of two steps: purification of the arsenic charge and the actual growth of single crystals. Both procedures are done in a composite quartz container which is sketched in the inset of fig. 1. Three distinct sections are identified: the loading region, intermediate transfer region and the growth region (bomb). The first two sections serve as purification stages which are subsequently discarded and the actual growth of the crystals is done in the bomb. In order to minimize any contamination of molten arsenic from the container wall, the bomb is made from 32 mm diameter very high purity synthetic quartz ingot (Suprasil) [6] which has a total metallic impurity of about 1 ppm. In comparison, previously used clear quartz from rock crystals has a total metallic impurity in the range 20–30 ppm. One end of the quartz ingot is first softened and pulled into a conical shape. The ingot is then drilled out with a tapered diamond head so as to produce a 25.4 mm inside diameter cylinder with a 75° conical tail section. The wall thickness of the bomb is slightly over 3 mm. The inside surface is diamond polished to produce a very smooth surface. The tapered section serves two important purposes: it acts as a nucleation center for crystal growth and, since arsenic expands on solidification, it helps to reduce the strain on the crystal by allowing it to expand upward along the axis of the bomb. Since the rest of the container is never exposed to temperatures above 500°C and it does not come in contact with *molten* arsenic, it is not necessary to use a rather expensive synthetic quartz for its construction, Amersil T08 Commercial Grade was used instead for this purpose. On assembling the container, it was cleansed in chromic acid, followed by a thorough rinsing in distilled water and, finally, steam cleaned.

High purity arsenic, Cominco Grade 6-9, in the form of small irregular pieces, was placed into the loading region of the container which was evacuated to 5×10^{-6} Torr. While continuing pumping, the arsenic charge is heated up for 1–2 h at 350°C using a small tubular heater. The vapor pressure of oxides on the surface of arsenic is high enough at this temperature and these are pumped away and condensed in a liquid nitrogen trap. The container is then sealed off just above the loading region. The next step consists of two sublimation distillation transfers, first into the intermediate section and subsequently into the bomb. The transfer into the intermediate section is achieved by inserting the quartz container into a horizontal tubular furnace so that arsenic is located at its hottest point (about 500°C). The temperature gradient along the tube then drives arsenic vapor towards the other end of the container. A small heater, placed just behind the intermediate section is adjusted so that all vapor condenses in the intermediate section. The dark grey oxide residue left behind in the loading section is separated by collapsing the quartz tube a few centimeters from the distilled arsenic. At this stage, arsenic already has a silvery and lustrous appearance. To further purify the arsenic charge, a second distillation is effected by again inserting the quartz tube into the furnace and arranging the temperature gradient so that arsenic vapor condenses inside the bomb. One can still observe minute traces of oxides left behind in the intermediate section thus demonstrating the benefits of a double distillation used in our procedure. The bomb is separated from the remainder of the quartz tube by collapsing the tube just above the neck of the bomb and a small hook is made at its top. For the purpose of crystal growth we have used a 1 m long, 5 cm diameter single zone tubular furnace. The temperature profile of the furnace was carefully determined using a Model 2190A Fluke digital thermometer monitoring a Pt/Pt–13%Rh thermocouple and is shown in fig. 1. The power of the furnace was adjusted and automatically controlled so that its highest temperature was 818°C, about 5°C above the melting point of arsenic. The quartz bomb was suspended on a thin steel wire which was attached on top of the furnace to a variable speed motor and the bomb was brought to a position just above the point of the maximum temperature and left there for several hours. Subsequently, the motor was started and the bomb was slowly lowered (10 mm/h) through the region of maximum temperature. After the first pass, the ingot consisted of typically two to four large crystals. On repeating the growth procedure the entire ingot becomes one large, shiny, single crystal. Altogether, 8 such passes

have been done on our two arsenic ingots. The rationale behind the multiple passes was to further purify the arsenic by segregating remaining impurities at the ends of the ingot as the solid–liquid interface moves through. Since only a part of the ingot is molten at each instant of the growth process, as the bomb is lowered through the region of maximum temperature, impurities cannot redistribute effectively during the next growth pass.

3. Sample preparation and results

After the completion of the final pass, the bomb is removed from the furnace and carefully opened. This is done using the procedure similar to that described in ref. [3]: the bomb is placed and firmly pushed into a plasticine pad and two opposing cuts are made along its axis with a narrow (0.5 mm) diamond wheel operating at a high speed. The depth of the cuts is gradually increased until a thin quartz shell remains which prevents the diamond wheel from touching the arsenic ingot. The boule is then easily split apart by inserting a screw-driver into the cuts. Since arsenic does not adhere strongly to quartz, the ingot usually pops out free at this stage. The crystal should be protected from prolonged exposure to air by storing in a desiccator; otherwise, it will soon form an oxide layer. Orientation of the arsenic boule is done by the Laue back reflection technique. A special three-axis goniometer is used which can be transferred from the X-ray generator to a Servomet spark-erosion machine. For both our arsenic boules the cleavage plane (plane perpendicular to the trigonal (111) axis) lies at about 40° from the axis of the ingot. Spark erosion is done with the slowest speed setting to minimize damage to the crystals. We find it preferable to use a thin copper blade electrode rather than a continuous wire which leaves small steps on the cut planes. Samples oriented with their long axis along the binary or bisectrix direction were cut with lengths of up to 30 mm. We also succeeded in cutting up to 12 mm long samples oriented along the trigonal axis, the direction of extremely easy cleavage. To prevent cleavage, a cross section of around 4×4 mm^2 was

chosen, rather than the 2×2 mm^2, typical of our binary-oriented samples. After cutting, any surface damage can be easily removed by etching for about 3 s in a mixture of 1 part HF + 1 part HNO_3 followed rapidly by rinsing in distilled water. After this procedure samples regain their shiny, silvery appearance and are protected from moisture and oxygen by storing in a desiccator or vacuum.

As we have already noted, the most reliable indicator of purity and quality of metallic (semi-metallic) samples is the residual resistance ratio, RRR. We have made measurements of RRR on several samples cut from different sections of the ingot. Samples cut from end-regions of the ingot had RRR in the range 2000–3000, values already substantially better than achieved previously. The samples of best quality, however, were prepared from the mid-section of the ingot; their RRR's were in the range 4000–5500. Systematic difference between the quality of samples cut from the end-regions and the mid-section of the ingot is most probably due to minute traces of impurity segregated near the ends of the crystal. If so, it would demonstrate the benefit of multiple passes used in our technique. We should like to stress that no annealing process was done on any of our samples. It is conceivable that, after a suitable heat treatment, the residual resistance ratios would be even higher.

Investigations of transport properties on these very high quality arsenic crystals are now in progress in our laboratory.

References

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