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Preparation of heavily doped *n*-type Ge–Si thermoelectric alloys

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Germanium–silicon alloys doped with phosphorus were prepared in vacuum by rapidly pouring the molten alloy into cooled copper moulds containing the phosphorus dopant. Without any further treatment, the ingots are milled into powder of grain size ($L \leqslant 5\,\mu$m) and hot pressed. It is shown that a high degree of homogenization of the alloy constituents can be obtained in the final compacts, thus eliminating the need for zone-levelled starting material. It is also shown that this work is in agreement with the plastic flow model of sintering known as the Mackenzie–Shuttleworth–McClelland model. Electrical measurements indicate that the dopant is effectively and uniformly incorporated into the alloy.

1. Introduction

Germanium–silicon alloys possess good thermoelectric properties at high temperature. There are certain features of these alloys, e.g. wide liquidus/solidus separation, low distribution coefficient and low diffusion coefficients, that make the preparation of homogeneous alloys difficult and to prepare homogeneous single crystals, zone-levelling techniques [1, 2] must be employed. Phonons of long wavelength are scattered at grain boundaries and this effect is most pronounced in Ge–Si alloys [3–6]. As a result of this, hot pressing techniques were developed to produce fine-grained compacts [7–10]. The question arises as to the nature of the starting material for the powder and whether it is necessary to use highly homogeneous zone-levelled single crystals only to reduce them to fine powder, or could a degree of inhomogeneity be tolerated. McVay *et al.* [7] used chill-cast n-type alloys for their starting material, while Savvides and Goldsmid [9] used rapidly quenched alloys. In both cases homogeneous fine-grained compacts have been obtained indicating that homogenization is taking place at somewhat accelerated rate.

We have recently reported the hot pressing of isothermally solidified p-type Ge–Si alloys [10] and obtained a high degree of homogenization even though the starting material had germanium-rich regions at the bottom of the ingot. While the isothermal techniques are suitable for alloys doped with high vapour pressure dopants, it would be difficult to reduce the dopant losses in the case of alloys doped with phosphorus. For this reason rapid cooling of the melt in cooled moulds containing the dopant, in this case phosphorus, were used to produce the starting alloys. This paper deals with rapid cooling of n-type Ge–Si alloys and their subsequent hot pressing to produce homogeneous fine-grained compacts. The hot-pressing data are examined to test the plastic flow model for the sintering of these alloys.

2. Experimental procedure

2.1. Rapid casting of n-type alloys

The use of this technique affords the separation of the molten alloy and the dopant as the latter is contained in the mould, and both come into contact at the moment of pouring. The top melting unit is shown in Fig. 1 and consists of a graphite susceptor (1) which also acts as crucible support. The crucible (2) is made of high-purity silica and both the susceptor and the crucible incorporate a hole at the bottom (3) to allow pouring of the melt. This hole is plugged by a silica tube (4) which also houses the thermocouple (5) used for temperature control. The graphite/silica assembly is surrounded by graphite felt (6) and an alumina tube (7) to minimize radiative heat loss. The silica plunger (4) is attached to a remotely operated electromechanical release mechanism (8) to facilitate pouring. The entire assembly is enclosed inside a silica/stainless steel vacuum-tight enclosure (9).

The casting unit is located directly below the top melting unit. This consists of a stainless steel water-cooled enclosure inside which the massive copper moulds are placed. The temperature of the mould is sensed by a thermocouple located directly below the mould. The temperature of the water is maintained at 285 K and is not allowed to rise above 290 K before pouring, to stop dopant evaporation. To stop the alloy reacting with the mould, a thin-walled silica insert is used to line the mould. The entire system is connected via a liquid nitrogen trap to the vacuum system which consists of a rotary pump/diffusion train capable of giving a vacuum of better than 10^{-5} torr. The seven-turns r.f. coil (10) is placed outside the silica tube and this is connected to a 30 kW, 365 kHz r.f. generator. Temperature-control is via a closed loop using a thermocouple/temperature programmer/controller, to within ±0.5 K.

The system also incorporates an inert gas purifier capable of producing argon gas with an impurity level

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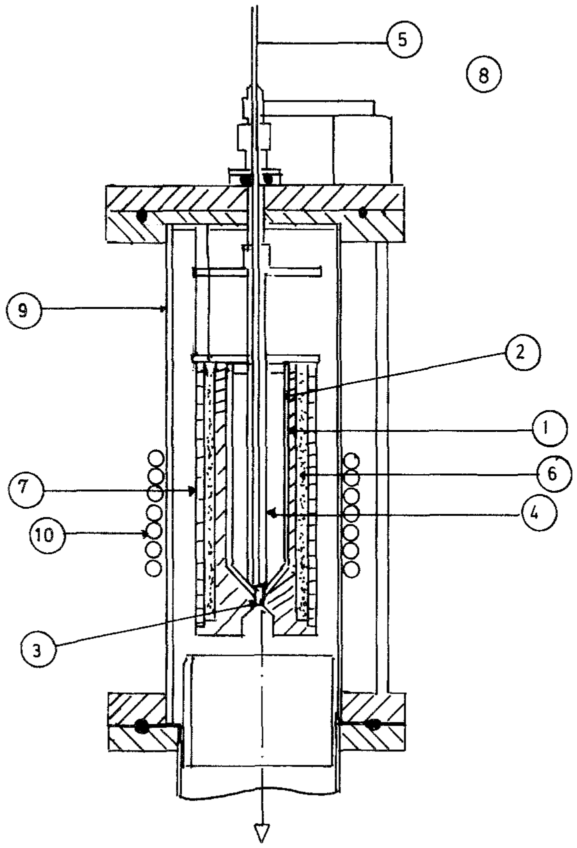

Figure 1 Top melting unit. 1, Graphite susceptor; 2, crucible; 3, bottom hole; 4, silica plunger; 5, thermocouple; 6, graphite felt; 7, alumina tube; 8, remote-control electromechanical release mechanism; 9, silica/stainless steel vacuum-tight enclosure; 10, seven-turn r.f. coil.

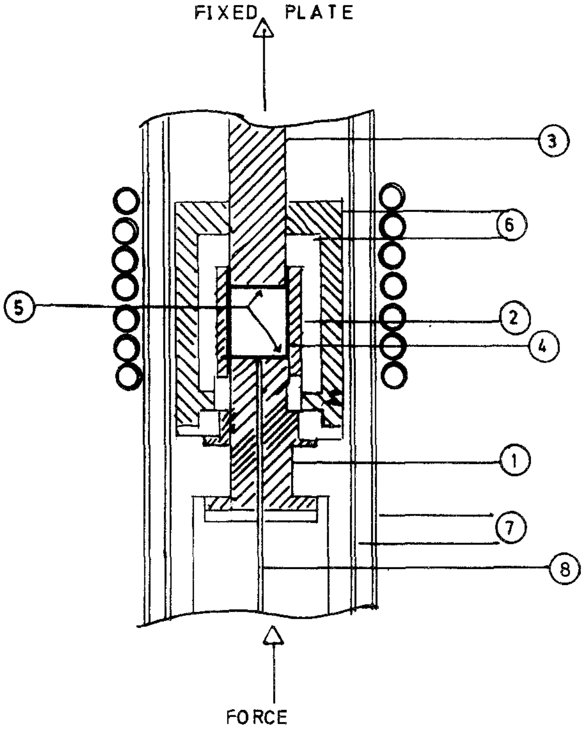

Figure 2 Schematic arrangement of hot press and die assembly. 1, Bottom plunger; 2, die cylinder; 3, top plunger; 4, 5, graphite liner; 6, susceptor; 7, silica; 8, thermocouple.

not exceeding 1 p.p.m. The purity of the gas is monitored by a miniature micromass gas analyser. A typical run consists of melting a charge of the appropriate elemental silicon and germanium weight fractions with impurity levels not exceeding 2 p.p.m. The charge weight is about 6×10^{-2} kg and is melted under a blanket of argon at atmospheric pressure. The charge is held at 50 to 100 K above the melting point to allow r.f. stirring for about 30 min, followed by pouring the charge through the bottom hole on to the mould containing the phosphorus. When the molten alloy strikes the phosphorus, it is immediately vaporized and penetrates the melt above it to within the solubility limit in the alloy.

2.2. Alloy milling and powder grading

Full details of this process have been reported elsewhere [10]. Containers and balls of agate are used to contain the ingot and a planetary mill is used for a period of 60 min. Grading is accomplished using precision-made nickel screens supported on stainless steel frames. The aperture range (L) is from 5 to 100 μm. To assist sieving, a liquid vehicle (high-purity ethanol) is used and this is separated from the powder by evaporation. The use of planetary ball mill reduces the ingot into powder of 80% with ($L \geqslant 30\,\mu$m) and the remainder is divided into fractions predominantly in the $L \leqslant 5\,\mu$m range.

2.3. Hot pressing

Again full details of this process can be found in a previous publication [10] with the notable replacement of the alumina-sheathed thermocouple by a platinum-sheathed one. To eliminate problems associated with cold-junction compensation, a type B thermocouple (Pt-30% Rh/Pt-6% Rh) was used. The hot press is shown schematically in Fig. 2. The pressing was conducted in vacuum of 10^{-5} torr using graphite-lined TZM dies of 25×10^{-3} m diameter. A maximum load of 9.2×10^4 kgf is used at a temperature of 1338 K for a period of 60 min. The vacuum system, temperature control and method of heating are the same as those mentioned earlier for the casting unit.

3. Analytical procedure

For a specimen of regular shape, density determination was made by weighing, and volume calculation from external dimensions. For an irregular shaped specimen, the method of hydrostatic weighing was used. Extensive use was made of metallographic techniques to reveal the structure of the alloys. The specimens are usually polished to a finish of 0.25 μm using diamond paste and etched in CP4a solution. Precise lattice parameter values were obtained using a vertical powder diffractometer with unfiltered cobalt radiation. The diffracted beam is monochromated using a curved graphite monochromator. The values of the lattice parameter are corrected using a Nelson–Riley function.

4. Electrical measurements

Resistivity measurements were carried out on a four-probe d.c. apparatus using appropriate corrections for specimen shape. Extensive use was made of the Seebeck coefficient measurements using the hot-probe technique (1.5 mm probe size). Carrier concentration measurements were carried out on a bridge-shaped

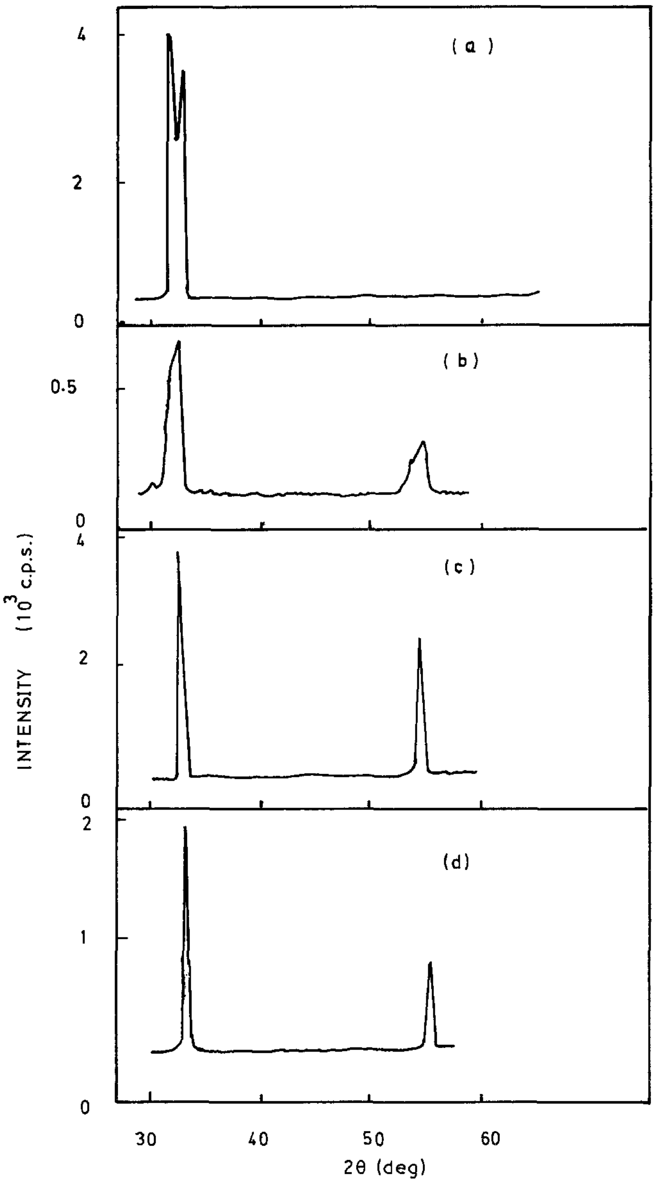

Figure 3 X-ray diffraction pattern using Co$K\alpha$ radiation, 40 kV, 20 mA. (a) Cast alloys; (b) alloy powder, $L < 5\,\mu$m; (c) hot pressed, $L < 5\,\mu$m; (d) silicon standard.

sample ultrasonically cut, using a.c. excitation and lock-in a.c. Hall-voltage detection. Specimens for electrical measurements were lapped and polished to a finish of 70×10^{-9} m using precision lapping equipment.

5. Results and discussion

Phosphorus has what is known as retrograde solubility in silicon, i.e. the solubility limit increases with decreasing temperature. The solubility limit of phosphorus in silicon is reported [11, 12] to be 0.43% at 1473 K, 0.5% at 1273 K and 0.45% at 1173 K. The solubility of phosphorus in germanium shows a similar trend with the maximum solubility of 0.4% at 873 K falling to 0.1% at 1173 K. All the percentages refer to atomic fraction. The amount of phosphorus used in our experiments was in excess of the solubility limit to allow for evaporative loss during initial contact with the melt. The choice of rapid cooling was made so as to reduce the time required to traverse the liquidus/solidus separation and thus avoid supercooling [13] and development of dendritic structure. Attempts were made to incorporate the phosphorus using diffusion methods. This route had to be abandoned as diffusion rates are slow to affect heavy doping of the alloys.

Metallographic examination of a longitudinal section of the whole ingot showed no dendritic structure except at the very top layer (last to solidify). The structure consists of a matrix of homogeneous Ge–Si alloy with small isolated germanium-rich areas. No continuous grain boundaries could be identified, suggesting that the entire ingot may be made up of one single grain with low-angle subgrain boundaries. X-ray diffraction from a section parallel to the mould axis (Fig. 3a) showed two strong peaks located at 31.79° and 32.75° 2θ, respectively. This suggests that the (1 1 1) plane is lying almost parallel to the axis of the ingot, and the absence of any other reflection confirms our metallographic observation that the entire ingot is a single crystal. The existence of the two (1 1 1) peaks corresponds to the matrix and the germanium-rich islands, respectively. No attempt was made to work out the lattice parameter from this pattern as the deviation of the (1 1 1) plane from the surface examined by X-ray is not known in absolute terms. Fig. 3b shows the same pattern but in powder form ($L \leqslant 5\,\mu$m) and as can be seen, the peaks are

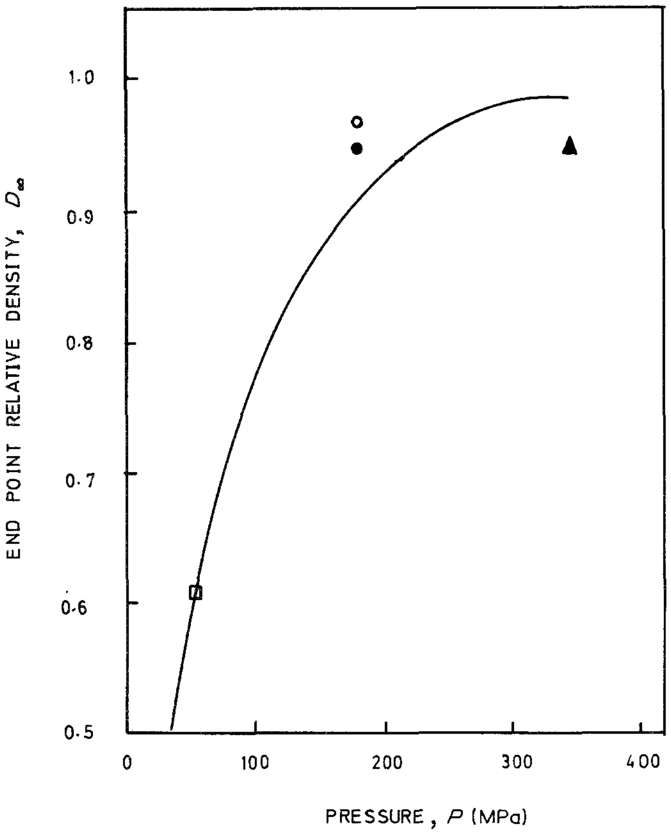

Figure 4 Graphical representation of the plastic flow equation after Savvides and Goldsmid [9]. (▲) [16]; (□) [9]; (○) [10]; (●) present work.

fairly wide, indicating the existence of continuous change in composition rather than the existence of a phase with a distinct composition. The latter would be shown as a resolved doublet or triplet depending on the number of phases present.

Fig. 3c shows the diffraction pattern of a hot-pressed compact of $L \leqslant 5\,\mu\text{m}$. The line width indicates that the entire disc (24 mm) is of single composition. Comparison of this pattern with that of pure silicon (Fig. 3d) shows that the full width at half maximum of both is almost identical. This comparison is valid, as Fig. 3d is from elemental silicon which should not show any broadening due to the existence of segregation. Lattice parameter calculation from Fig. 3c and fitting this value into the data of Dismukes *et al.* [14] gave an average composition for the area of the disc irradiated by X-rays of 49.47 at % Ge, which is very close to the nominal composition of the alloy of (Ge$_{0.5}$–Si$_{0.5}$). It would therefore appear that hot pressing contributes significantly to homogenization and that compositions close to those intended can be produced, provided that the whole ingot is milled.

Cross checking of X-ray patterns from different sieved fractions showed no significant difference indicating that no preferential milling, as indicated by Lefever *et al.* [7], had occurred. A further check on the homogeneity of the hot-pressed compact was carried out using Seebeck coefficient measurements with a probe diameter of approximately 1.5 mm. Twelve readings were taken which gave an average value of $170\,\mu\text{V}\,\text{K}^{-1}$ and a standard deviation of $2.2\,\mu\text{V}\,\text{K}^{-1}$, and this represents 1.3% variations of at least the dopant distribution. This figure of 1.3% is within the accuracy of the method. Other electrical measurements gave a carrier concentration of $5.2 \times 10^{25}\,\text{m}^{-3}$ at a resistivity value of $3.42 \times 10^{-5}\,\Omega\text{m}$.

Savvides and Goldsmid [9] showed that the sintering of these alloys is by a plastic flow mechanism often referred to as the Mackenzie–Shuttleworth–McClelland model [15, 16]. Data from widely differing Ge–Si compositions and from different works [9, 10, 17] fit this model well indicating its validity. Fig. 4 shows a graphical representation of the plastic flow equation together with points taken from previous reports [9, 10, 17] for approximately the same pressing temperature of 1350 K. For this alloy the measured density of the compact is $3.677 \times 10^3\,\text{kg}\,\text{m}^{-3}$, compared with $3.8903 \times 10^3\,\text{kg}\,\text{m}^{-3}$ for the bulk density, giving a relative end-point density (D_∞) of 94.5% which represents a close fit to the line representing the equation of plastic flow [9].

While sintering is via a plastic flow mechanism, it appears that diffusion is greatly enhanced under pressure resulting in a highly homogeneous hot-pressed compact. The structure of the hot-pressed compact did not show apparent grain growth on metallographic examination.

From this work, it is concluded that a relatively inhomogeneous starting alloy which is probably unsuited for use in thermoelectric devices in bulk form, can be turned into fine-grained highly homogeneous compacts, thus significantly eliminating the need for zone-levelled material.

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