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METHOD OF FABRICATION OF GERMANIUM-SILICON ALLOY

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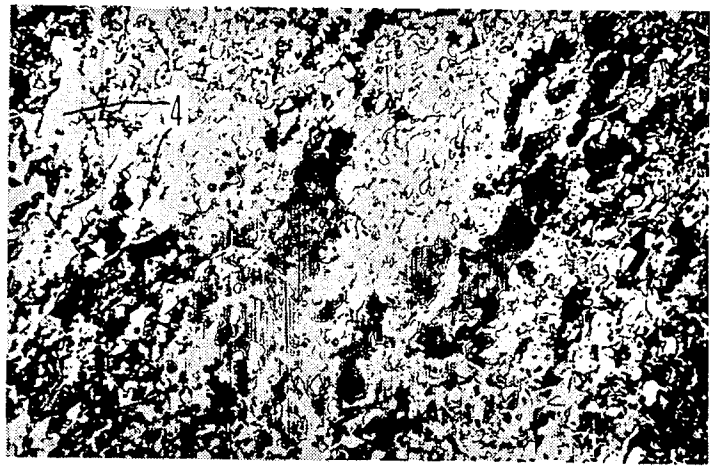



FIG.1

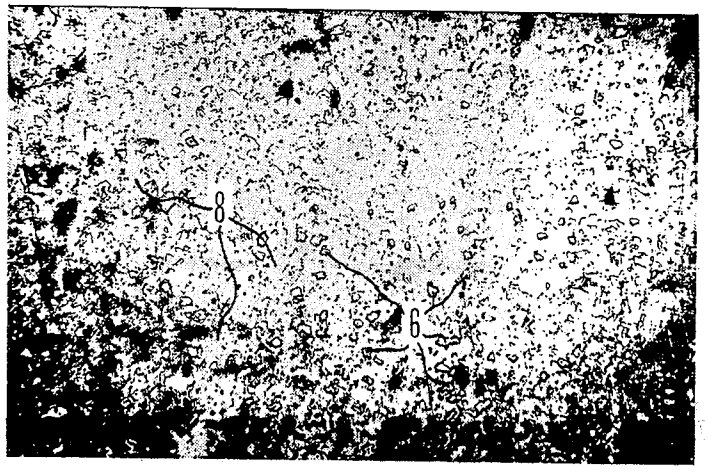



FIG.2

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# METHOD OF FABRICATION OF GERMANIUM-SILICON ALLOY

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## ABSTRACT OF THE DISCLOSURE

A method for preparing a doped germanium-silicon alloy. The method consists of mixing germanium and silicon and thereafter melting the mixture by application of high frequency energy from a source which is displaced relative to the mixture of germanium and silicon at a rate sufficient to obtain good homogenization of the mixture. The doping material may be added to the germanium and silicon prior to mixing or during the melting step.

This invention relates to a method of preparation of germanium-silicon alloy with incorporation of dope and applicable especially to the thermoelectric conversion of power.

The electrical output of thermoelectric generators is dependent on the proportion of dope which is incorporated with the germanium-silicon alloy and on the thermal conductivity of said alloy; this output is at maximum value in the case of the figure of merit Z which is given by the formula:

$$Z=\frac{\alpha^2\overline{o}}{K}$$

wherein:

$\alpha$=Seebeck coefficient
$\overline{o}$=electrical conductivity
K=thermal conductivity

and it can therefore be visualized that this output will be dependent on the thermal conductivity which must be as low as possible; said thermal conductivity is determined by the respective concentrations of the two constituents and above all by the degree of homogeneity of the solid solution since, in the field with which we are concerned (approximately 50 to 70 atom percent of Si), it is difficult to produce an homogeneous solid solution. This is due to the low values of diffusion coefficients of each constituent of the alloy.

Consequently, in order to obtain an alloy which is as homogeneous as possible, it is necessary at the time of melting to await the establishment of equilibrium between the two constituents within the liquid phase; and it is for this reason that, up to the present time, melting processes have been performed at very low speed in order to remain within conditions which are close to equilibrium. Thus, in these processes as in the process of zone-melting with isothermal solidification, it is hardly possible to exceed a rate of preparation of a few millimeters per hour.

This output also depends on the proportion of dope incorporated with the alloy which determines the electrical resistivity and the Seebeck coefficient. However, this time-consuming method of preparation results in the volatilization of the dope and does not make it possible to retain a sufficiently high proportion of dope in the final alloy.

The invention is directed to a method of preparation of a germanium-silicon alloy which is more rapid than existing processes and which makes it possible to attain sufficient proportions of dope without difficulty.



To this end, the method according to the invention consists in mixing fragments of germanium and silicon in the desired proportions, in melting said mixture at high frequency as a result of the relative displacement of an induction coil and of said germanium-silicon mixture and in cooling the mixture which is obtained, the melting process being performed at a frequency and at a rate of displacement which are sufficiently high to obtain good homogenization of the mixture.

The relative displacement of the induction coil and of the mixture is carried out by means of a movement of translation of the induction coil over the mixture which remains stationary or alternatively by means of a movement of displacement of the mixture itself whilst the induction coil remains motionless. The relative displacement must be sufficiently rapid to ensure that the mixture of the different constituents is correct. The effect of the rate of displacement necessarily depends on the power of the generator and on the coupling which is formed. The rate of displacement must be at least equal to 15 millimeters per minute: depending on the power of the generator, speeds of up to 165 millimeters per minute can be attained but will preferably be of the order of 100 millimeters per minute under normal operating conditions.

The relative displacement is carried out in both directions and homogenization is improved by effecting a number of successive passes. The number of passes thus effected in back and forth motion has an influence on the homogeneity of the alloy which is formed; when the number of back-and-forth passes exceeds 40, the influence is less marked, so that the operation usually consists in effecting 30 to 40 passes in back-and-forth motion.

The melting process is carried out at a frequency which is at least equal to 4 mHz. and preferably of the order of 5 to 6 mHz. It is apparent that this method permits of higher speeds of preparation than those which are permitted by methods of the prior art. Such speeds are permitted by the fact that it is not necessary to ensure complete equilibrium between the germanium and the silicon since the stirring action produced by the electromagnetic forces and by convection ensure the homogenization of the alloy.

Moreover, since the process can be performed without achieving conditions of equilibrium, the requisite proportions of dope can be readily introduced, such proportions being usually within the range of 50 to 500 p.p.m. in the case of antimony and indium. The dope is introduced either in the initial mixture or between two successive passes.

The processes of the prior art made use of starting constituents in the form of fine powder which, in the case of products having such a high degree of hardness, cannot readily be obtained without appreciable contamination. On the contrary, the process in accordance with the invention makes it possible to employ coarsely crushed germanium and silicon as starting material.

The method makes it possible to obtain germanium-silicon alloys which have a particularly low thermal conductivity while permitting of relatively rapid processing; thus, in one hour and thirty minutes, it has been possible to obtain ingots having a thermal conductivity K which is less than 30 mw./°/cm. This result can be considered very satisfactory.

Tests have shown that the product obtained has a low thermal conductivity (less than 30 mw./°/cm.) when the phase which is rich in germanium is dispersed to a sufficient extent. When said phase which is rich in germanium is not sufficiently dispersed, it has an appearance

similar to that which is shown in FIG. 1, which corresponds to a relatively high thermal conductivity of the order of 100 mw./°/cm. In this figure, which corresponds to an alloy containing 50% by weight of germanium, the insufficiently-dispersed phase which is rich in germanium is designated by the reference numeral 4. On the other hand, FIG. 2 shows a germanium-silicon alloy having the same composition in which the high germanium-content phase (reference 6 in the figure) is well dispersed, and the thermal conductivity of which is equal to 25 mw./°/cm. Moreover, in this case, the compositions of the two phases have become more similar, in that the phase (6) which is rich in germanium contains 50% by weight of this metal and the phase (8) which is low in germanium contains 45% by weight of germanium.

The preparation of the alloy is carried out in a conventional high-frequency zone-melting apparatus designed for use either in an inert atmosphere such as argon or helium, for example, or in a high vacuum of the order of $10^{-7}$ mm. Hg. The germanium and silicon are crushed into fragments of a few decigrams, for example, and are placed in the hollowed-out portion of a water-cooled sole or hearth; the aggregate is melted by means of an induction coil which is displaced along the mixture.

The heating is carried out at a sufficiently high frequency which is at least equal to 4 mHz. and which is preferably in the vicinity of 5 to 6 mHz. in order to ensure that the ratio of power applied to the alloy to power applied to the hearth reaches a sufficient value. At these frequencies, the stirring action produced on the liquid by the electromagnetic forces and by convection is very substantial and is sufficient to ensure good homogenization of the alloy; however, it would be possible if so desired to achieve a further improvement in homogeneity by making use of ultrasonics.

When it is desired to produce the alloy in the form of rods, a fairly wide molten zone approximately 3 to 4 centimeters in width is formed and displaced by means of the induction coil at a sufficiently high speed (15 to 100 mm./minute) in order that the different constituents should be well mixed.

If the induction coil is moved at too low a speed, the time of solidification of the zone located behind the molten zone is too long, with the result that the alloy thus produced has two distinct solid phases having an appearance which is similar to that shown in FIG. 1.

The thermoelectric properties of the germanium-silicon alloy thus obtained are checked by measuring its thermal conductivity.

The nature of the hearth has an influence on the thermoelectric properties of the alloy which is formed; in fact, at the time of melting, the metal of which the hearth is made tends to contaminate the alloy. After a number of tests, a hearth of copper-chromium alloy has been adopted, in which the proportion of chromium contained in the alloy does not exceed 5 p.p.m.

There will now be described without implied limitation three examples of practical application of the method according to the invention.

## EXAMPLE 1

10 g. of germanium and 10 g. of silicon were melted by moving the induction coil at a speed of 50 millimeters per minute in twenty passes back and forth; there was thus obtained an ingot of 18.2 g., 10 centimeters in length and 25 centimeters in diameter, which was formed of an alloy containing 50% by weight of germanium. The thermal conductivity which was measured at 300° C. was 37 mw./°/cm.; the time of preparation was approximately 100 minutes.



## EXAMPLE 2

10 g. of germanium and 10 g. of silicon were melted by moving an induction coil at a rate of 100 millimeters per minute in 20 passes back and forth; there was obtained an ingot of 18 g. of alloy having the same dimensions as in Example 1 and containing 50.5% by weight of germanium. The thermal conductivity as measured at 300° C. was 31 mw./°/cm., and the preparation time was 60 minutes.

## EXAMPLE 3

10 g. of germanium and 10 g. of silicon were melted at an average speed of displacement of the induction coil of the order of 70 millimeters per minute in 26 passes back and forth; there was obtained an ingot of 17.6 g. of germanium-silicon alloy containing 48% by weight of germanium having the same dimensions as in Example 1. The thermal conductivity as measured at 300° C. was 20 mw./°/cm. and the time of preparation was approximately 185 minutes.

What I claim is:

1. The method of preparing a doped germanium-silicon alloy, comprising mixing germanium and silicon, melting said mixture by application of energy having a frequency at least equal to 4 mHz. from a high frequency energy source which is displaced relative to said mixture at a rate of displacement at least equal to 15 millimeters per minute to obtain good homogenization of the mixture, and adding a doping material to said germanium and silicon at a point prior to the completion of the melting step.

2. The method of claim 1, wherein the mixture is melted by application of energy having a frequency of about 5 to 6 mHz.

3. The method of claim 1, wherein the mixture is stationary and the high frequency energy source is displaced relative thereto.

4. The method of claim 1, wherein the high frequency energy source is stationary and the mixture is displaced relative thereto.

5. The method of claim 1, wherein the high frequency energy source is displaced in successive opposite directions relative to the mixture.

6. The method of claim 1, wherein the doping material is added to the germanium and silicon prior to the mixing of said germanium and silicon.

7. The method of claim 1, wherein the doping material is added to the germanium and silicon mixture after the melting step has commenced.


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RICHARD O. DEAN, Primary Examiner

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