March 3, 1964 R. M. JEPSON 3,122,827

POLYCRYSTALLINE ARTICLE AND METHOD FOR MAKING SAME

Filed Aug. 4, 1960

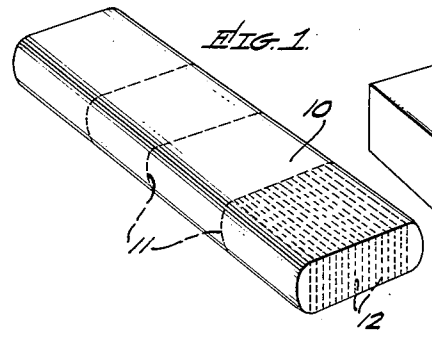


FIG. 1.

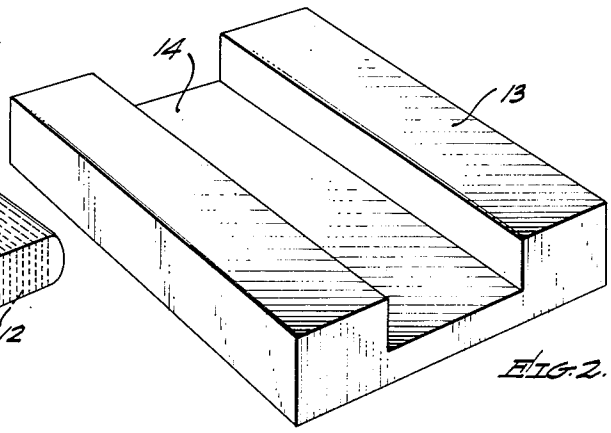


FIG. 2.

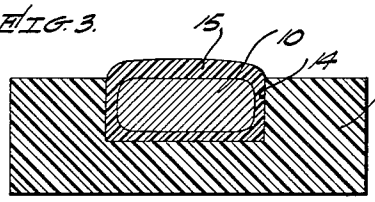


FIG. 3.

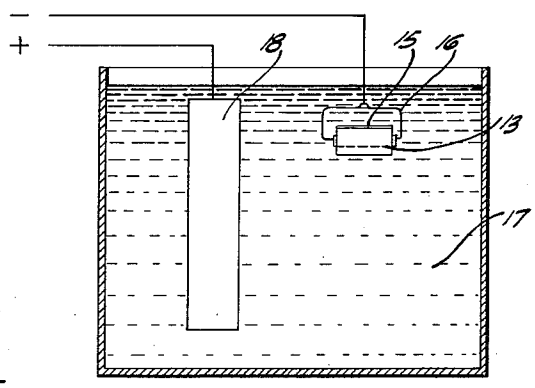


FIG. 4.

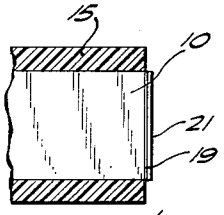


FIG. 5.

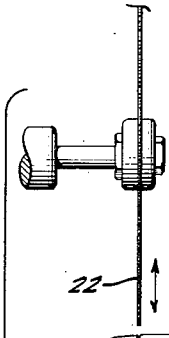
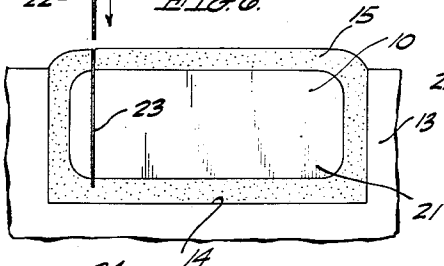


FIG. 6.



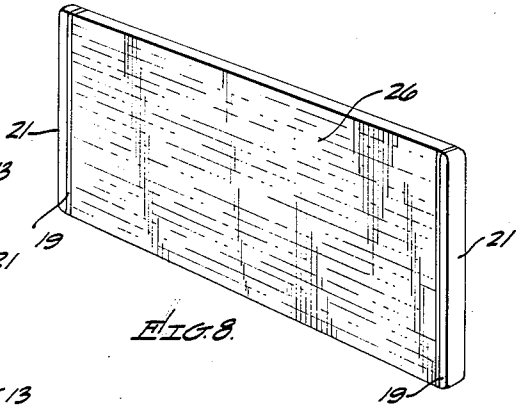


FIG. 8.

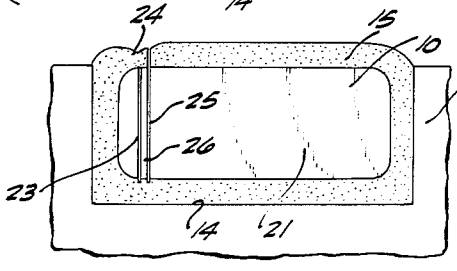


FIG. 7.

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POLYCRYSTALLINE ARTICLE AND METHOD FOR MAKING SAME

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5 Claims. (Cl. 29—423)

This invention relates to a method for producing polycrystalline articles and to the article thus produced, and more particularly to the slicing of polycrystalline materials into thin wafers or strips.

The invention has particular utility, and is herein specifically described, in connection with the slicing of semiconductor materials, such as bismuth telluride, into thin strips or wafers for use in the manufacture of thermoelectric junctions for cooling, heating, generation of electricity, and the like. It is understood, however, that the process of the invention is applicable to the cutting of other types of crystalline materials used for other purposes and is not to be limited to the cutting of specific semiconductor materials or for specific application to thermoelectric junctions.

There has been much contemporary activity in the use of semiconductors in thermoelectric junctions. Bismuth telluride and similar materials have been used extensively for this purpose in the form of polycrystalline rods or blanks in which the crystals extend longitudinally of the rods. In the formation of thermoelectric junctions, the rods or blanks are cut to the desired length and attached, fused, welded or otherwise secured at their ends to sections of copper bars or plates to form spaced hot and cold junctions. Such rods have a substantial cross sectional area, which not only increases the size and cost of construction for a given number of junctions in an assembled unit, but also, due to high current and low voltage requirements, adversely affects the design and performance where a large temperature differential is to be maintained betwen the hot and cold junctions with relatively small heat transfer.

To permit operation of the device at a desirable low current and relatively high voltage, it has therefore become necessary to cut or slice the rods or blanks into relatively thin strips or wafers which may be used in an assembly having a large number of junctions without necessitating the high cost and high bulk of the assembly. This cutting or slicing operation is very difficult to perform due to the necessary crystalline organization in and the fragile characteristics of the semiconductor material. During cutting, the drag of a cutting wheel is itself sufficient to fracture the thin strips and, even if the strips are successfully cut, they are so fragile that they are extremely difficult to handle in a subsequent assembly operation.

It is accordingly one important object of the present invention to provide a method of producing polycrystalline bodies by which such bodies can be successfully cut or sliced into thin strips or wafers capable of being handled and assembled into a completed unit without disintegrating.

Another object of the invention is to provide a cutting method in which the ends of a body or rod blank to be cut are first reinforced and secured together by a metallic coating preferably formed by plating the ends of the sections and then by a coating of solder before the cutting operation.

A further object of the invention is to provide a cutting method in which the body or rod section is first potted with each cut through the potting material and rod being sealed or filled at its open side before a subsequent cutting operation to support the thin strips of material formed by the cuts during the cutting operation.

Still another object of the invention is to provide a polycrystalline article of manufacture having means for reinforcing the crystalline structure thereof.

Other and further important objects of this invention will become apparent from the disclosures in the following detailed specification, appended claims and accompanying drawing, wherein:

FIGURE 1 is a perspective view of a rod with transverse and longitudinal lines of cut therein being illustrated by dotted lines;

FIG. 2 is a perspective view of one example of a holder which may be used in the cutting process;

FIG. 3 is an enlarged transverse sectional view through the rod as assembled and retained in the illustrated holder by a potting material;

FIG. 4 is a diagrammatic view illustrating one form of a plating step in the process;

FIG. 5 is a partial sectional view through an end of the rod or blank and potting material, illustrating the plated and soldered blank ready for cutting;

FIG. 6 is an end elevational view illustrating a first step in the cutting operation;

FIG. 7 is a view similar to FIG. 6 illustrating a succeeding step in the cutting operation; and

FIG. 8 is a perspective view of a typical completed crystalline article.

A rod, as shown at 10 in FIG. 1, which is to be sliced into a series of thin strips or wafers may be of any desired cross section and any desired length and is of a polycrystalline structure with the crystals running longitudinally thereof. An example of a typical rod has been illustrated as having flattened opposed surfaces of a thickness equal to the desired width of the strips or wafers and of an indeterminate length as it is obtained from a supplier. In this connection, it is to be understood that the stock material may be of any desired or necessary configuration without departing from the spirit and scope hereof.

For forming the rod into strips or wafers, it is first transversely cut, as indicated by the dotted lines 11, into sections having a length equal to the desired length of the strips or wafers. Thereafter, each of the strips is longitudinally sliced by a series of spaced parallel cuts, indicated by the dotted lines 12, to form a plurality of thin strips or wafers in which the crystals run longitudinally thereof.

For cutting, the rod 10 may be supported, for example, in a supporting member 13, one form of which is typically shown in FIG. 2, which may be made of any desired type of relatively rigid material. The holder 13 is preferably formed from a reinforced thermosetting plastic material which sets up relatively hard and rigid although any other desired type of material having the requisite strength and rigidity may be used. The holder is, for purposes of illustration, in the form of a generally rectangular section body with an elongated groove 14 formed in one surface thereof and of a size larger than the cross sectional size of the rod 10. The rod is supported in the holder, as shown in FIG. 3, as by potting material 15 which completely surrounds the peripheral surface of the blank and secures it in the groove 14 in the holder. Any of the conventional potting materials which will set up relatively hard may be used for this purpose, such as hard wax, shellac, or various thermoplastic or thermosetting resins. A material must be selected, however, which can be made flowable at a temperature well below the melting temperature of the crystalline rod blank so that the crystalline structure of the rod will not be damaged by elevating it to an excessively high temperature.

With the rod blank secured in the holder by the pot-

ting material, the transverse cuts may be formed by any conventional cutting method. Since the rod is well supported by the potting material and the holder, the transverse cuts may be made by sawing, although the preferred method is to use a diamond cutting wheel or similar cutting device. The transverse cuts are made through the rod blank, the potting material and the holder to leave short sections of rod blank securely potted in short lengths of the holder and with exposed planar ends thereof.

After the transverse cutting operation, the exposed ends of the rod blank are coated with a thin metallic coating. This may be accomplished by dipping the ends of the blank in molten bismuth, with care being taken to remove the rod from the bismuth before it becomes heated sufficiently to damage the crystalline structure. It is to be noted that the potting material acts as a mask during the plating, spraying or dipping operation. The coating may also be formed by spraying or chemical depositing; however, the preferred method is by electroplating, as illustrated in FIG. 4. Preferably before the plating operation, the planar ends of the blank are lightly abraded as by sand blasting to roughen them slightly and are then thoroughly cleaned. In this condition, the ends of the blank are receptive to the metal coating. The metal employed may be any metal capable of adhering to the blank and of accepting solder, with nickel being the preferred metal where spraying or plating is employed and bismuth being the preferred metal where dipping is employed.

For plating, as illustrated in FIG. 4, the ends of the blank are gripped by conductive tongs **16** and the entire assembly of holder, blank and potting material is immersed in an electroplating bath **17** as the cathode. An anode **18** of pure nickel or other metal to be plated is in the bath and is connected as a cathode in an electroplating circuit so that a plating of the metal will be formed on the exposed clean ends of the blank in the usual manner. The plating so formed may be quite thin in the nature of a flash plate and in the order of .0002 to .003 inch in thickness.

After plating or preliminary coating of the ends of the blank, a thin layer of solder is applied over the plating on the planar ends of the blank. Any solder, such as a standard lead-tin solder, may be employed which has a melting point below the melting point of the crystalline material and the solder may be applied in the usual manner by dipping the ends of the blank into the molten solder or by applying the solder with heated iron. The thickness of the solder is not critical, but is should be at least .002 inch and preferably does not exceed .020 inch.

After plating and soldering, the blank will appear, as shown in exaggerated detail in FIG. 5. The potting material will enclose the side walls of the blank with the exposed ends being covered by a thin metal plated layer **19** and an overlying layer of solder **21**. The composite layers of plated metal and of solder on each longitudinal end of the completed article serve several important purposes according to the invention. In the first place, they securely tie together the ends of the crystals in the blank, thereby substantially strengthening and reinforcing the crystalline blank and holding the crystals together after the blank has been cut into thin slices. Secondarily, the coating facilitates soldering of or otherwise attaching the slices into an assembly after they have been formed by the cutting operation. Also, the coatings serve as a barrier to migration of unwanted and undesirable substances into the crystalline material.

After the ends of the blank have been plated and soldered, the cuts **12** are formed therein, preferably by a diamond wheel as partially shown at **22** in FIG. 6, or other suitable cutting methods. An extremely thin wheel is employed so that the cuts may be as thin as possible to minimize wastage of the crystalline material which is quite expensive and also in order that the crystalline material may be formed into thin strips for the desired use.

It has been found to be important in the cutting operation that the wheel be moved in a straight line directly through the rod section, in the direction of the arrow shown in FIG. 6, without any component of movement of the entire cutting element parallel to the crystalline grain structure in the rod. It has been found that if the wheel is moved longitudinally of the grain structure, it tends to tear out the crystals so that the desired thin strips are destroyed in the cutting operation. However, if the cutting wheel is moved in a straight line through the blank, extremely thin strips, in the order of .010 inch in thickness, can successfully be cut. It will be noted from FIG. 6 that the wheel forms a straight cut **23** extending through the outer surface of the potting material **15** and completely through the blank into the lower layer of the potting material.

According to an important feature of the present invention, the open edge of the cut through the potting material is first sealed or filled before a second cut is made. This feature of the invention is illustrated in FIG. 7 wherein the open end of the completed cut is closed before a second cut parallel thereto is formed. When a thermoplastic potting material, such as a shellac-like material, is employed, this sealing may be effected by running a hot iron along the top of the cut to close the cut through the potting material, as illustrated at **24**. When a thermosetting potting material is employed, the edge of the cut may be filled with potting material of either a thermosetting or thermoplastic type to close the cut in a manner similar to that illustrated in FIG. 7. In either case, some of the potting material will ordinarily flow partially into the gap in the blank itself to support the portion of the blank adjacent to the cut during the second cutting operation.

After the open edge of the cut has been closed, as described, a second cut, illustrated at **25**, is formed in the same manner as the first cut parallel to and spaced therefrom a distance equal to the desired thickness of the strip or wafer. This will separate the blank into a thin, flat sided strip or wafer article **26** which is of the desired dimensions for the ultimate use thereof.

The second cut is then sealed or closed in the same manner as the first cut and additional cuts are formed in the same way to separate the blank into a plurality of strips or wafers, such as at **26**. After completion of all of the cutting operations, the potting material may be removed, as by dissolving it in a suitable solvent, to leave a plurality of strip or wafer articles ready for use.

It will be noted that the crystalline material, according to the present invention, is securely supported against any displacement during the cutting operation by the combination of the potting material and the metallic coatings **19** and **21** at the ends of the blank. Due to this supporting, the crystalline material can be cut or sliced in the manner described into thin strips or wafers. Even after the potting material is removed the strengthening and reinforcement provided by the metallic coatings **19** and **21** gives to the strips or wafers sufficient mechanical strength so that they can be handled in the subsequent assembling operations without being fractured or destroyed. Thus, by the present invention it is possible to reduce fragile crystalline structures to thin strips or wafers successfully and enables use thereof in a practical low current and relatively high voltage thermoelectric device.

The article thus formed by the steps of this process is illustrated in FIG. 8 and, as shown comprises the crystalline body having the crystals thereof generally oriented in a longitudinal direction. The ends of the individual crystals are thus supported and retained in their original configuration by the coating **19** and **21**. As shown, the article has planar outer surfaces that are smooth and regular. In actual practice, the layer of solder **21** may vary slightly in thickness throughout its length along the end of the article. Such variance is not particularly important and it will at least partially be eliminated when

the crystalline article is secured in position to form a thermoelectric junction.

While the present polycrystalline strip or wafer has been described as being produced from a blank that is first plated or coated with a material that will adhere to the crystalling material, with the coated blank thereafter having a layer of solder applied thereto, it is to be understood that some installational situations will permit the elimination of one or the other of the coatings. In the physical assembly of the slices or wafers and the attachment thereof to conducting elements such as copper bars or the like, it may be seen that the solder may be applied to the copper bars rather than the articles, and thereafter an attachment made to a simple plated or coated end surface of the crystalline articles. In another instance, the plating or coating step with either a liquid dip or a sprayed, plated or otherwise affixed layer of material may be eliminated and a coating of solder or other supporting and affixing material may be applied directly to an end surface of the crystalline body. In still a further instance, other suitable physical means may be employed for supporting the crystalline structure when formed into the slice or water configuration thereof. Upon such formation, it is possible to utilize suitable masking and to apply a plated or coated supporting means for the articles to the previously cut or formed crystalline bodies.

Having thus described the invention and the present embodiments thereof, it is desired to emphasize the fact that further modifications may be resorted to in a manner limited only by a just interpretation of the following claims.

I claim:

1. In a method of making wafers of semiconductor material having a width and length much greater than the thickness thereof and metal-coated on opposite ends but not on the faces, and having the crystalline grain structure extending lengthwise thereof, from an elongated flattened rod of semiconductor material having the crystalline grain structure extending lengthwise thereof, and having a width across the flats equal to the desired width of the wafers and a length equal to the desired length of the wafers, said method comprising the steps of:

(*a*) securing said rod of semiconductor material rigidly into a flat groove in an elongated supporting holder with one flat side in the bottom of the groove and the other flat side substantially flush with the top of the holder by surrounding said rod with a soluble potting material which sets up hard;

(*b*) reinforcing the crystalline grain structure of said semiconductor material by coating the exposed ends of said semiconductor material with metal;

(*c*) making a series of parallel cuts longitudinally through said semiconductor material to the bottom of said groove, filling each cut with said potting material and allowing it to harden prior to making the next cut, the spacing between said cuts being equal to the desired thickness of the wafers;

(*d*) and dissolving said potting material with a solvent to separate said wafers.

2. In a method of making wafers of semiconductor material having a width and length much greater than the thickness thereof and metal-coated on opposite ends but not on the faces, and having the crystalline grain structure extending lengthwise thereof, from an elongated flattened rod of semiconductor material having the crystalline grain structure extending lengthwise thereof, and having a width across the flats equal to the desired width of the wafers, said method comprising the steps of:

(*a*) securing said rod of semiconductor material rigidly into a flat groove in an elongated supporting holder with one flat side in the bottom of the groove and the other flat side substantially flush with the top of the holder by surrounding said rod with a soluble potting material which sets up hard;

(*b*) cutting said semiconductor material, said holder and said potting material transversely into sections having a length equal to the desired length of the wafers;

(*c*) reinforcing the crystalline grain structure of said semiconductor material by coating the exposed ends of said semiconductor material with metal;

(*d*) making a series of parallel cuts longitudinally through said semiconductor material to the bottom of said groove, filling each cut with said potting material and allowing it to harden prior to making the next cut, the spacing between said cuts being equal to the desired thickness of the wafers;

(*e*) and dissolving said potting material with a solvent to separate said wafers.

3. In a method of making wafers of semiconductor material having a width and length much greater than the thickness thereof and metal-coated on opposite ends but not on the faces, and having the crystalline grain structure extending lengthwise thereof, from an elongated flattened rod of semiconductor material having the crystalline grain structure extending lengthwise thereof, and having a width across the flats equal to the desired width of the wafers, said method comprising the steps of:

(*a*) securing said rod of semiconductor material rigidly into a flat groove in an elongated supporting holder with one flat side in the bottom of the groove and the other flat side substantially flush with the top of the holder by surrounding said rod with a soluble potting material which sets up hard;

(*b*) cutting said semiconductor material, said holder and said potting material transversely into sections having a length equal to the desired length of the wafers;

(*c*) abrading the exposed ends of said semiconductor material by sandblasting;

(*d*) reinforcing the crystalline grain structure of said semiconductor material by coating the exposed ends of said semiconductor material with metal;

(*e*) making a series of parallel cuts longitudinally through said semiconductor material to the bottom of said groove, filling each cut with said potting material and allowing it to harden prior to making the next cut, the spacing between said cuts being equal to the desired thickness of the wafers;

(*f*) and dissolving said potting material with a solvent to separate said wafers.

4. In a method of making wafers of semiconductor material having a width and length much greater than the thickness thereof and tinned on opposite ends but not on the faces, and having the crystalline grain structure extending lengthwise thereof, from an elongated flattened rod of semiconductor material having the crystalline grain structure extending lengthwise thereof, and having a width across the flats equal to the desired width of the wafers, said method comprising the steps of:

(*a*) securing said rod of semiconductor material rigidly into a flat groove in an elongated supporting holder with one flat side in the bottom of the groove and the other flat side substantially flush with the top of the holder by surrounding said rod with a soluble potting material which sets up hard;

(*b*) cutting said semiconductor material, said holder and said potting material transversely into sections having a length equal to the desired length of the wafers;

(*c*) abrading the exposed ends of said semiconductor material by sandblasting;

(*d*) reinforcing the crystalline grain structure of said semiconductor material by first electroplating the exposed ends of said semiconductor material with nickel and then tinning the plated ends of said semiconductor material with solder;

(*e*) making a series of parallel cuts longitudinally through said semiconductor material to the bottom of

said groove, filling each cut with said potting material and allowing it to harden prior to making the next cut, the spacing between said cuts being equal to the desired thickness of the wafers;

(*f*) and dissolving said potting material with a solvent to separate said wafers.

5. In a method of making wafers of bismuth telluride having a width and length much greater than the thickness thereof and tinned on opposite ends but not on the faces, and having the crystalline grain structure extending lengthwise thereof, from an elongated flattened rod of bismuth telluride having the crystalline grain structure extending lengthwise thereof, and having a width across the flats equal to the desired width of the wafers, said method comprising the steps of:

(*a*) securing said rod of bismuth telluride rigidly into a flat groove in an elongated supporting holder with one flat side in the bottom of the groove and the other flat side substantially flush with the top of the holder by surrounding said rod with a soluble potting material which sets up hard;

(*b*) cutting said bismuth telluride, said holder and said potting material transversely into sections having a length equal to the desired length of the wafers;

(*c*) abrading the exposed ends of said bismuth telluride by sandblasting;

(*d*) reinforcing the crystalline grain structure of said bismuth telluride by first electroplating the exposed ends of said bismuth telluride with nickel and then tinning the plated ends of said bismuth telluride with solder;

(*e*) making a series of parallel cuts longitudinally through said bismuth telluride to the bottom of said groove, filling each cut with said potting material and allowing it to harden prior to making the next cut, the spacing between said cuts being equal to the desired thickness of the wafers;

(*f*) and dissolving said potting material with a solvent to separate said wafers.

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